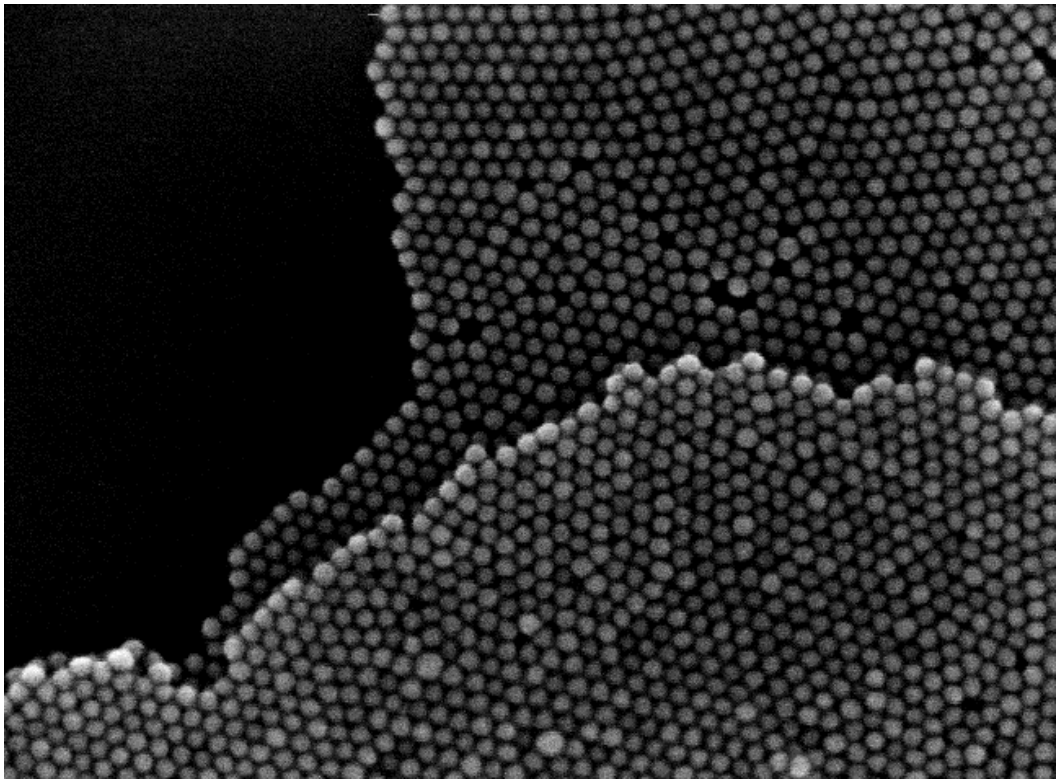
Self-Assembled Iron Oxide Thin Films at the Liquid-Air Interface



Leandra Boucheron • Candidacy Exam • September 4, 2013

Outline

- Introduction
- Techniques and Results
  - Grazing Incidence Diffraction (GID)
  - X-Ray Photon Correlation Spectroscopy (XPCS)
  - X-Ray Reflectivity (XR) and Grazing Incidence X-Ray Off-Specular (GIXOS)
- Future Work
  - Magnetic Effects
  - X-Ray Coherent Diffractive Imaging (CXDI)

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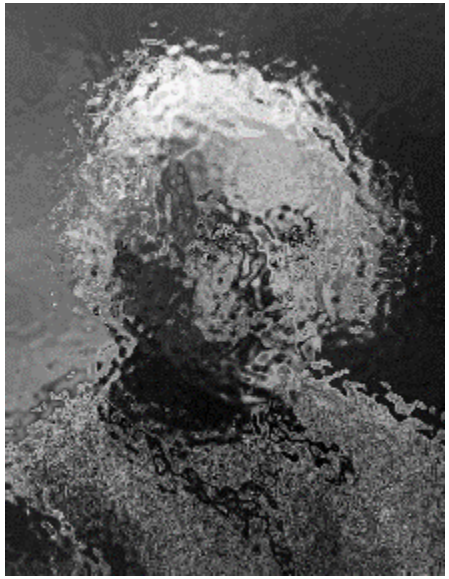
Introduction

You do not really understand something unless you can explain it to your grandmother.

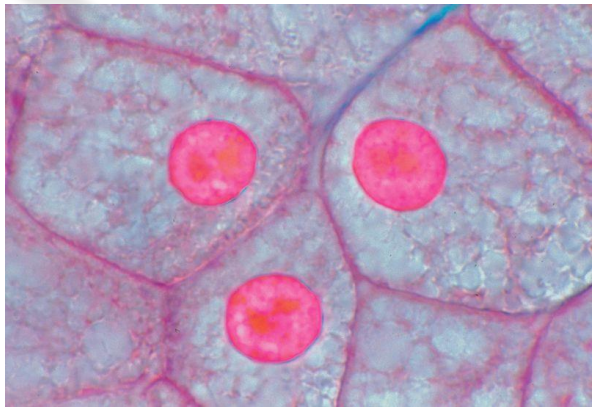


Leandra, a lot of things are nanotechnology. Tennis balls are nanotechnology. Even *humans* are nanotechnology!

1. Explain it to my committee
2. Explain it to my grandmother

Ways to Look at Small Things

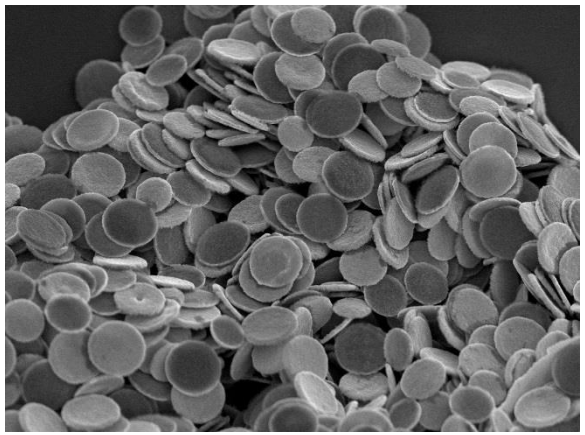
Optical Microscopy
>100nm



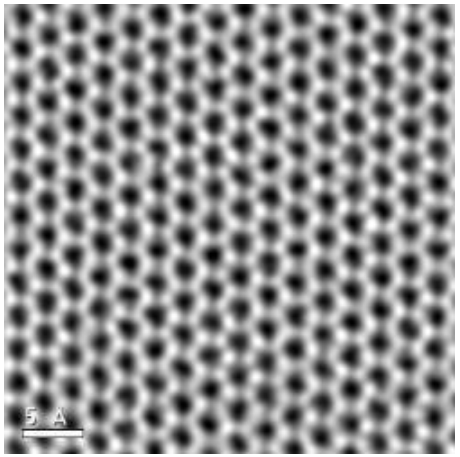
Diffraction Limit

$$d \sim \lambda$$

Scanning Electron Microscopy
>1nm



Transmission Electron Microscopy
>1Å

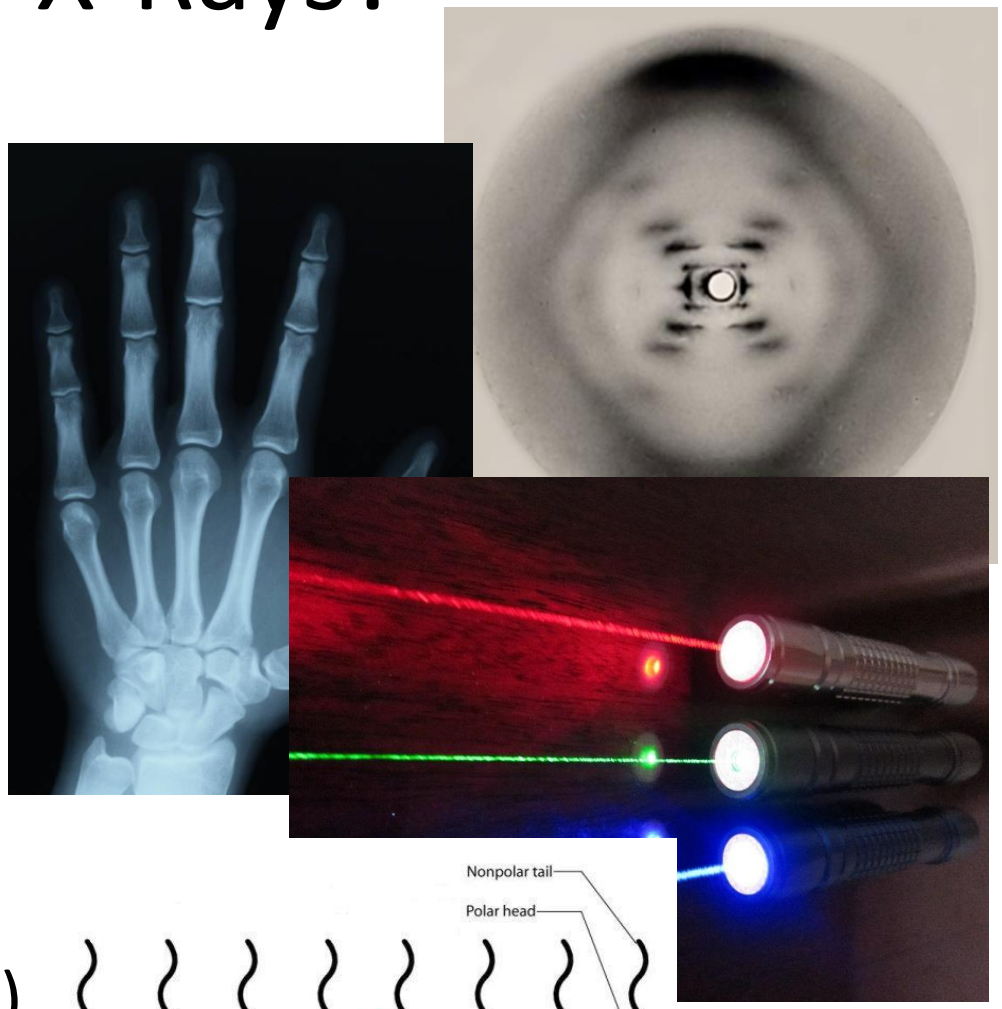


De Broglie Wavelength

$$\lambda = \frac{h}{p}$$

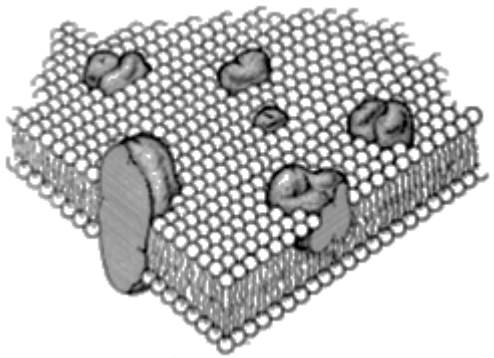
Why X-Rays?

- Wavelength (10pm-10nm)
- Penetrating
- Non-Invasive
- Global, Statistical Information
- *In situ* Studies
- Surface Sensitivity (GID)
- Coherence (XPCS)

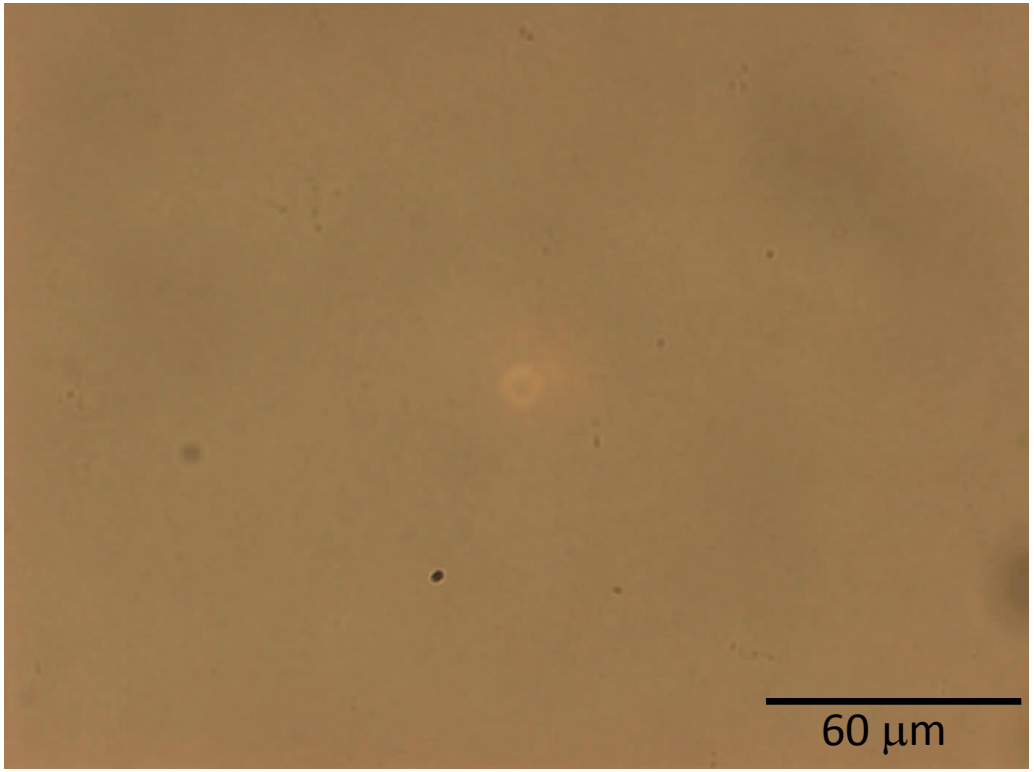


Interfacial Structures

- Optical Coatings
- Flexible Electronics
- Biomembranes



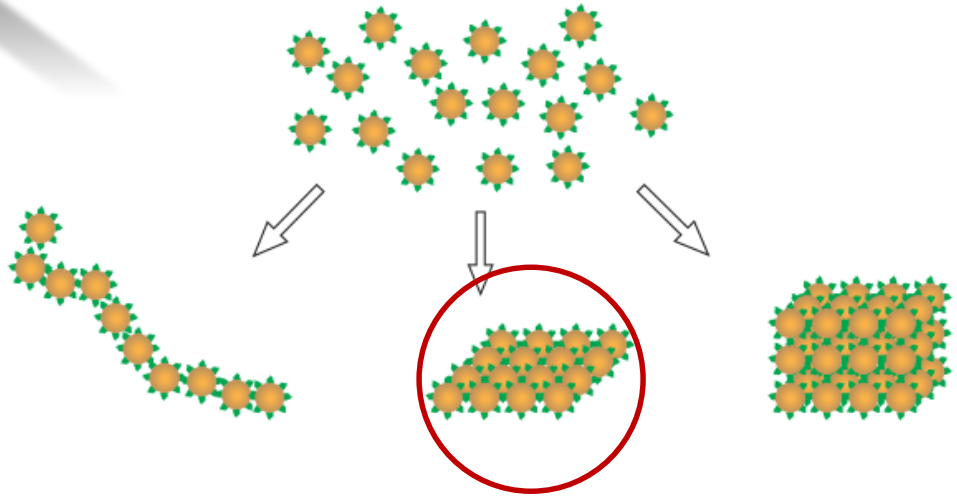
10nm iron oxide nanoparticle film during compression on liquid surface

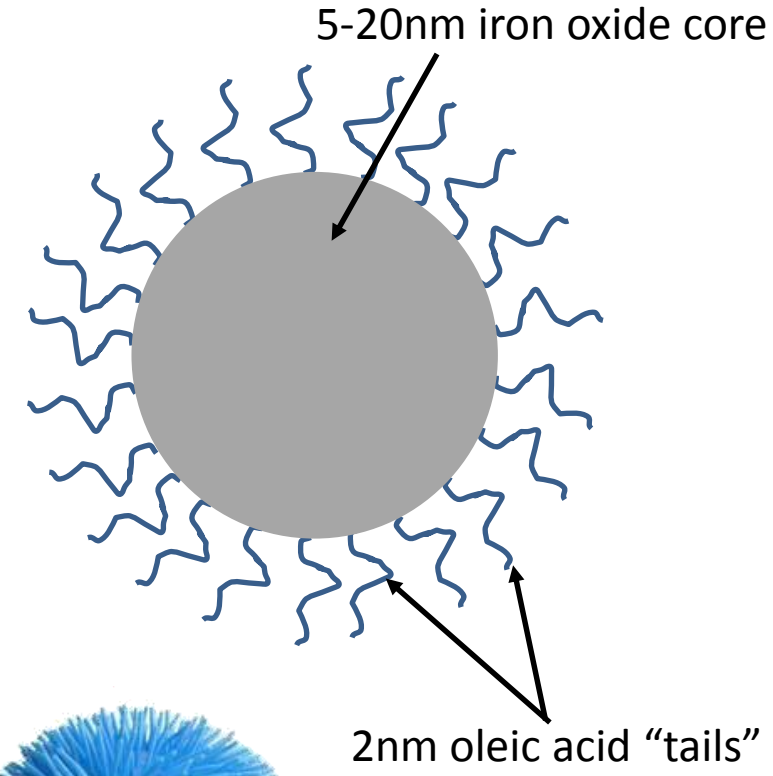


"There's no point in researching graphene any more, because the Nobel prize has already been awarded." –O.S.

Singer, S. J., & Nicolson, G. L. (1972). *Science*, *175*(23)

Liquid Surface Self Assembly

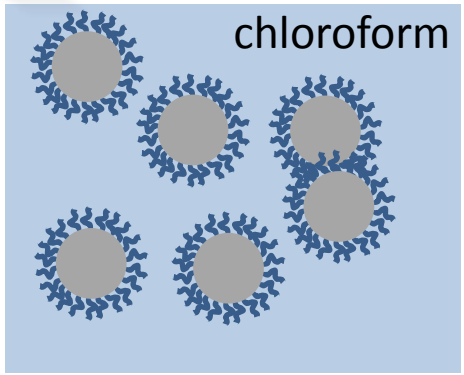


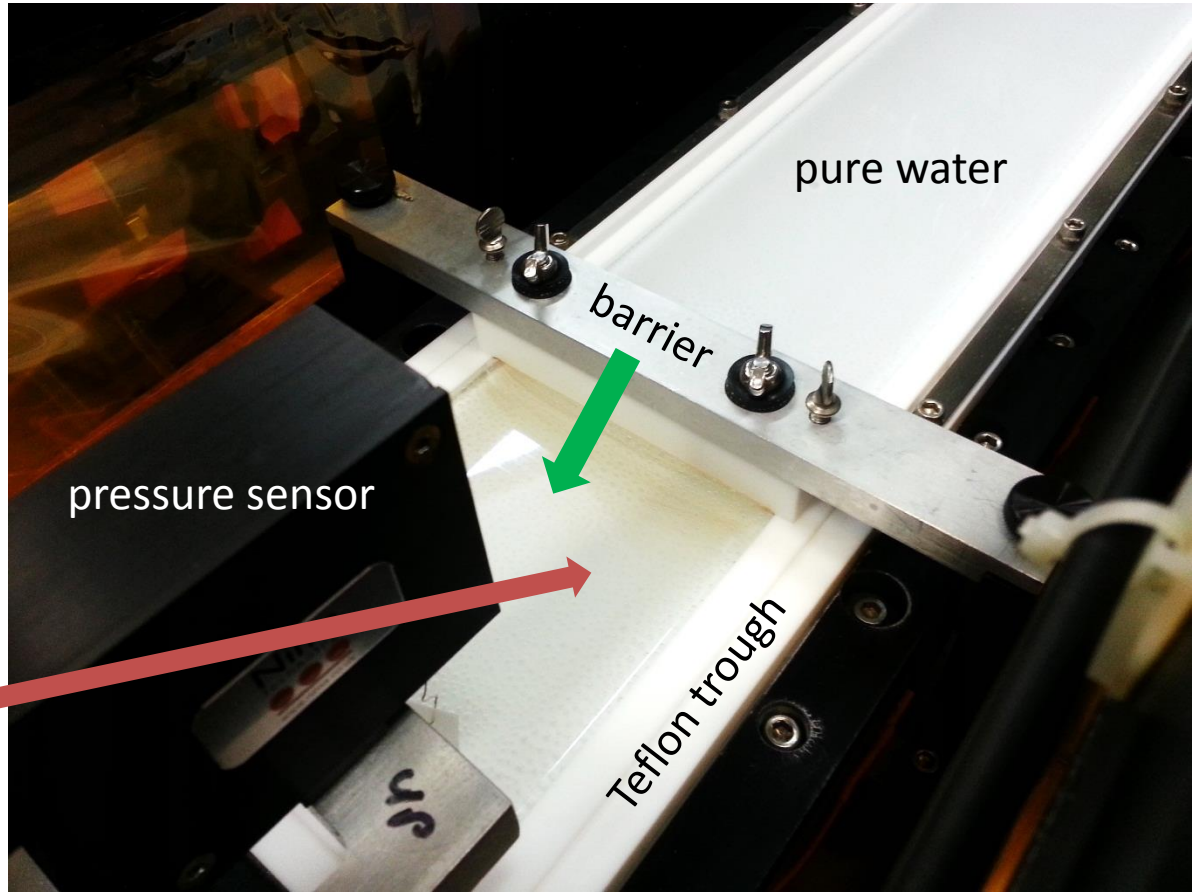


- Van der Waals Force
- Interfacial Forces
- Magnetic Interactions
- Electric Interactions

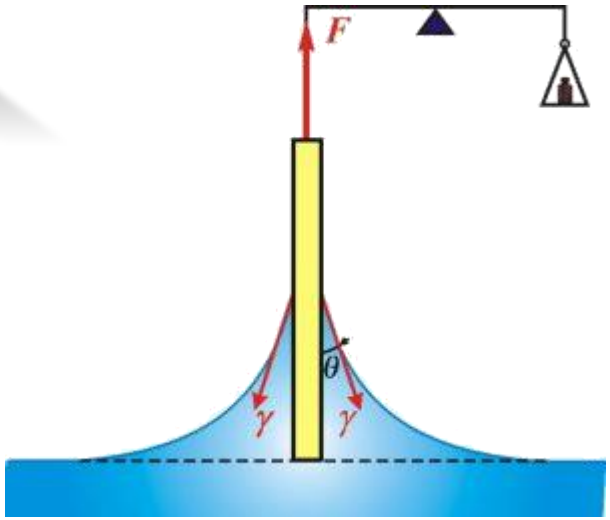
Nie, Z., Petukhova, A., & Kumacheva, E. (2010). *Nature nanotechnology*, *5*(1)

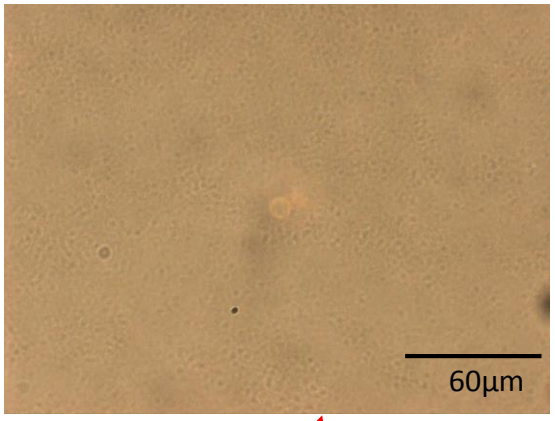
Langmuir-Blodgett Trough

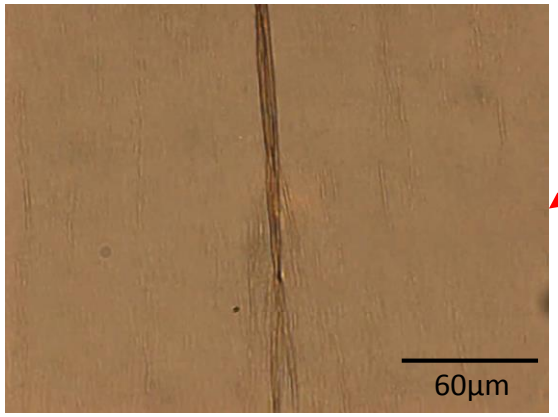


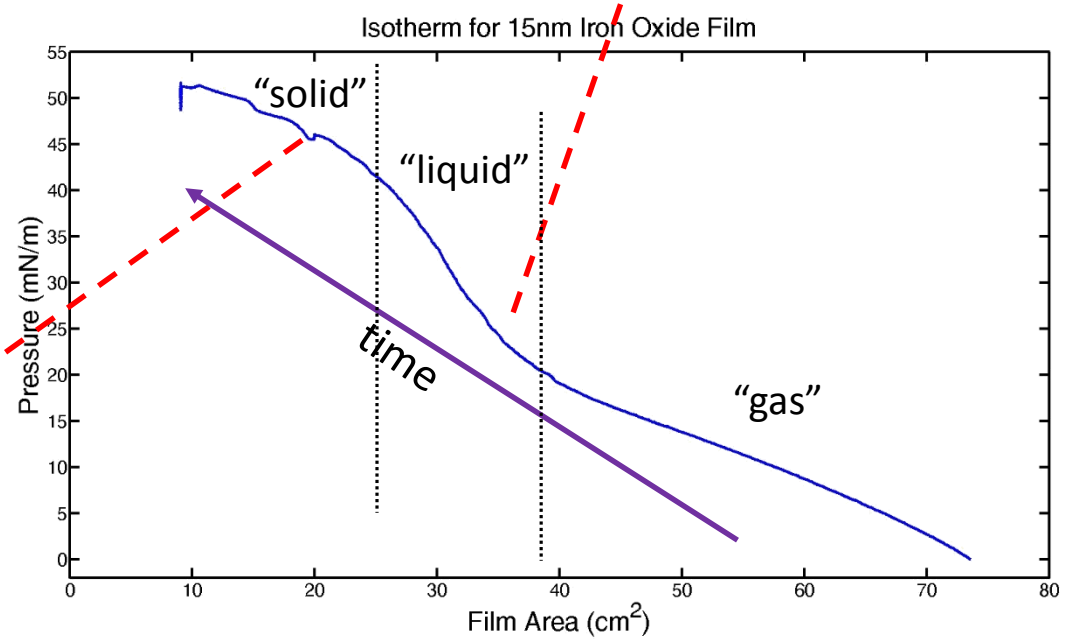


Isotherms


F
θ
γ
γ

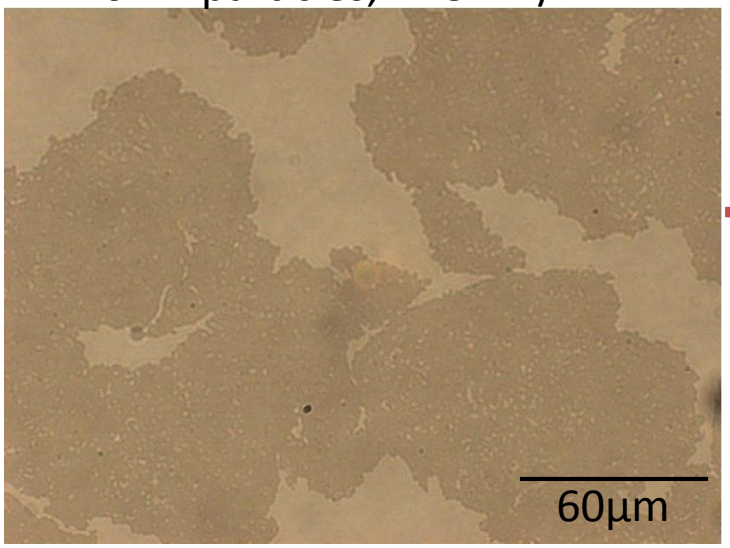

60µm


60µm

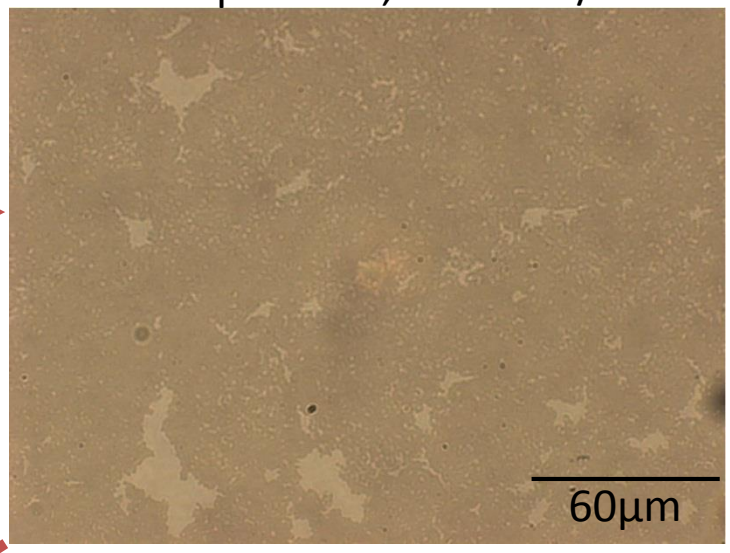

Isotherm for 15nm Iron Oxide Film
"solid"
"liquid"
"gas"
time
Pressure (mN/m)
Film Area (cm2)
0
5
10
15
20
25
30
35
40
45
50
55
0
10
20
30
40
50
60
70
80

The Macroscopic Picture

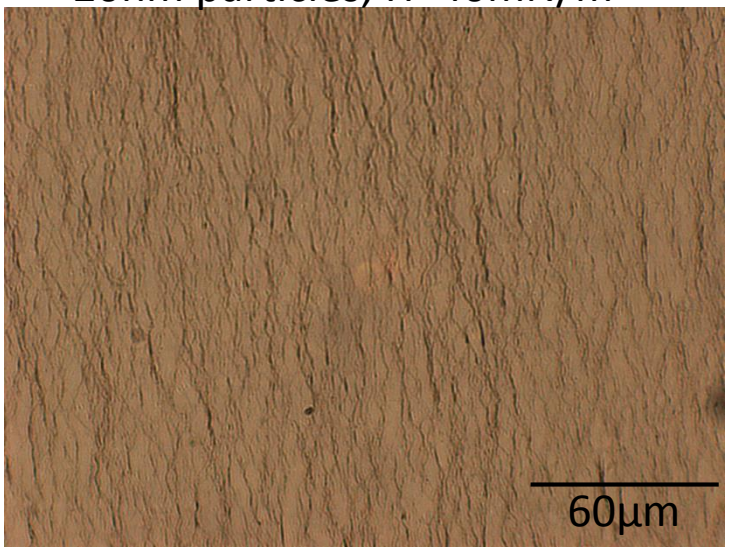
20nm particles, Π~5mN/m



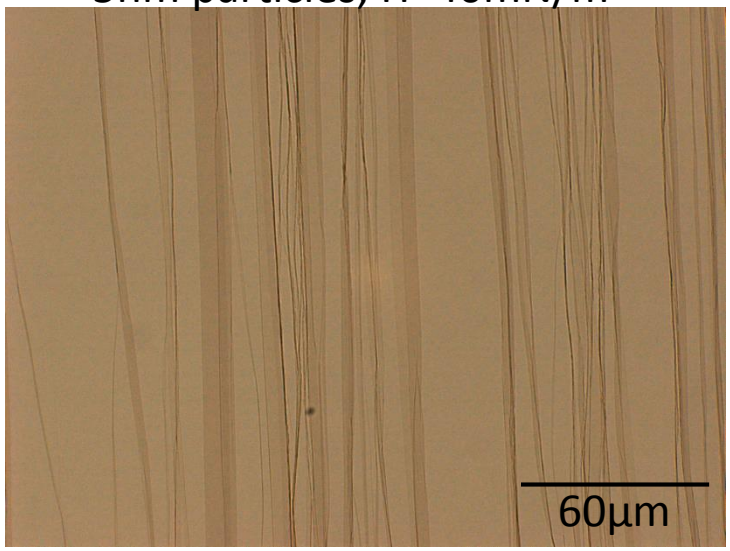
20nm particles, Π~15mN/m



20nm particles, Π~40mN/m



5nm particles, Π~40mN/m



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Full Characterization of Films

- In-Plane Structure
  - Grazing Incidence Diffraction (GID)
- In-Plane Dynamics
  - X-Ray Photon Correlation Spectroscopy (XPCS)
- Out-of-Plane Structure
  - X-Ray Reflectivity (XR) and Grazing Incidence X-Ray Off-Specular (GIXOS)

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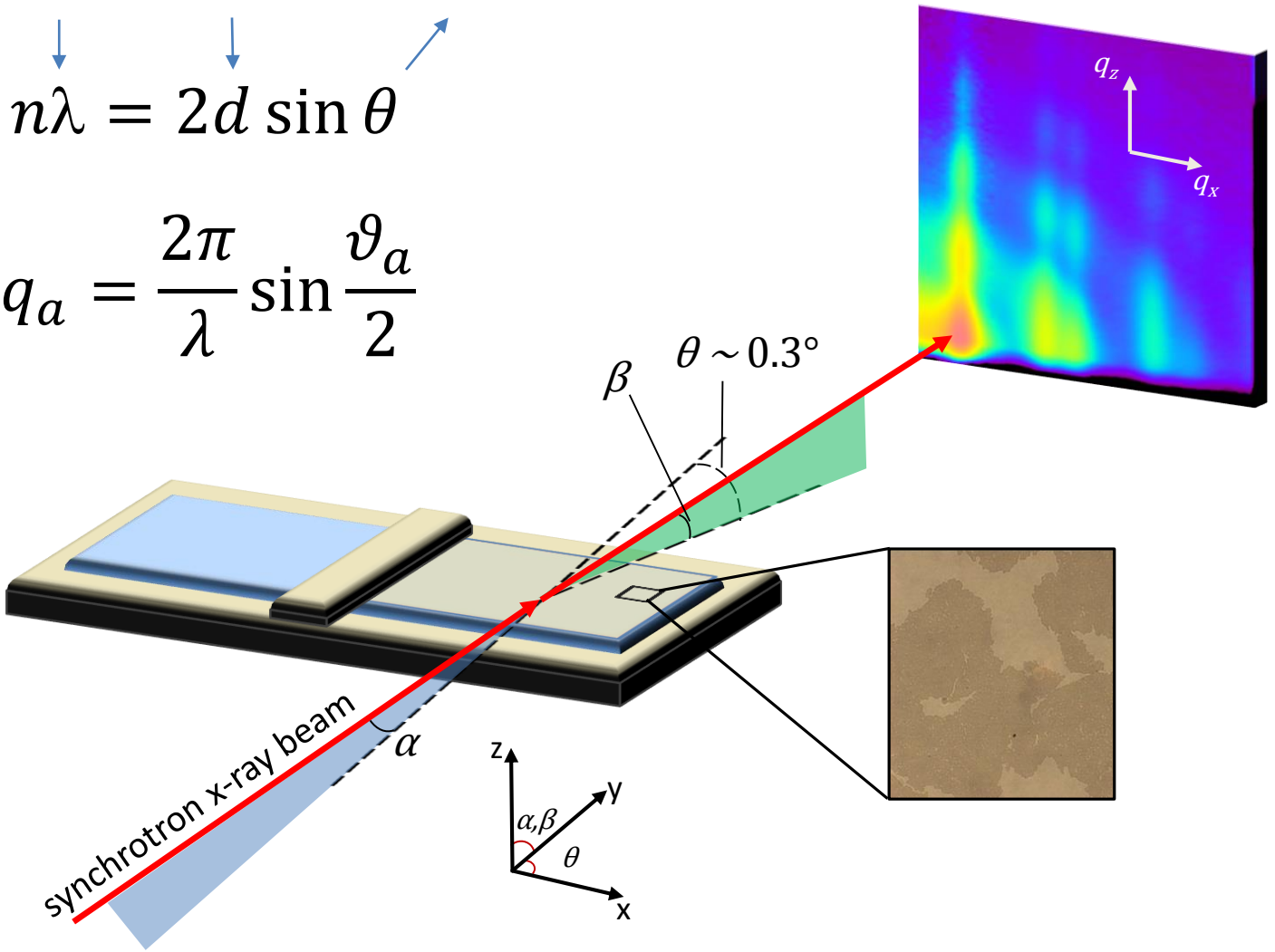
Grazing Incidence Diffraction (GID)

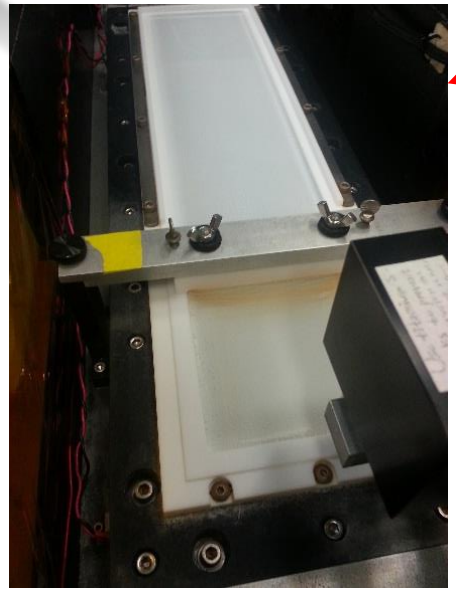
~1Å ~10nm ~0.3°

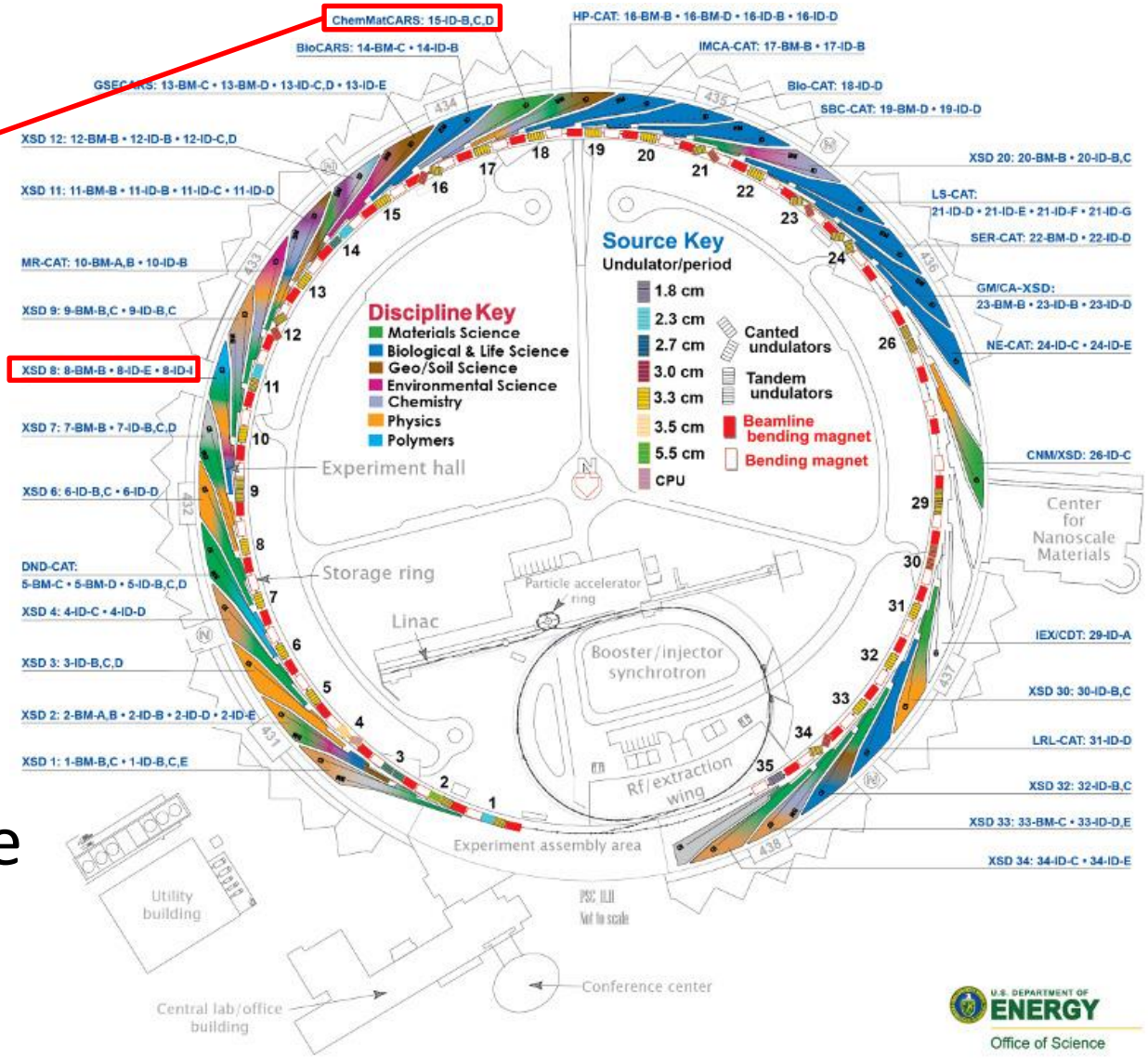
$$n\lambda = 2d \sin\theta$$

$$q_a = \frac{2\pi}{\lambda} \sin\frac{\vartheta_a}{2}$$



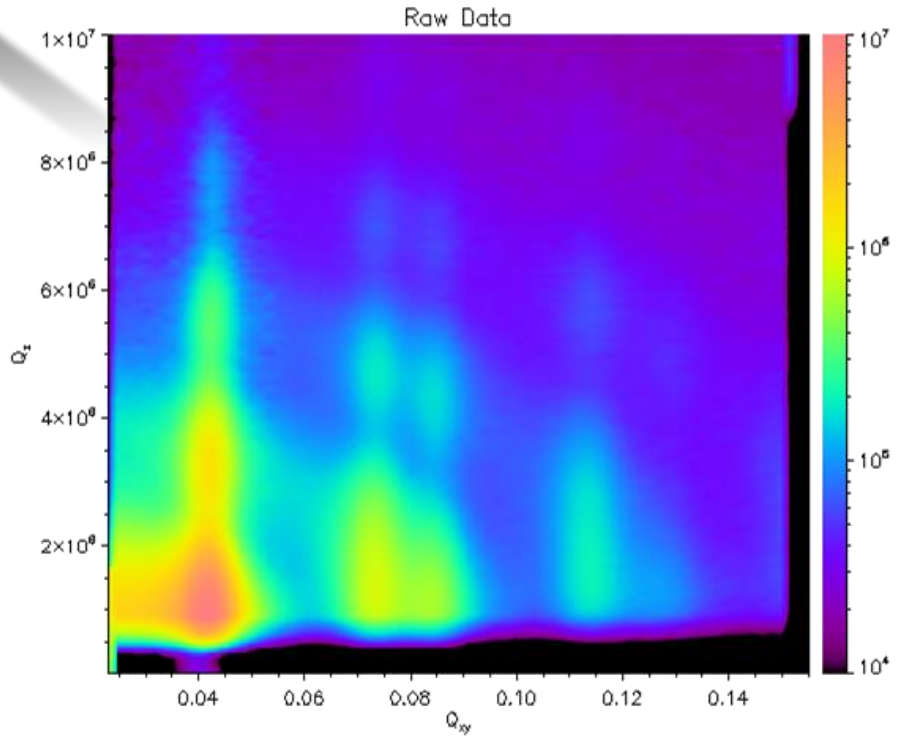
Experimental Location

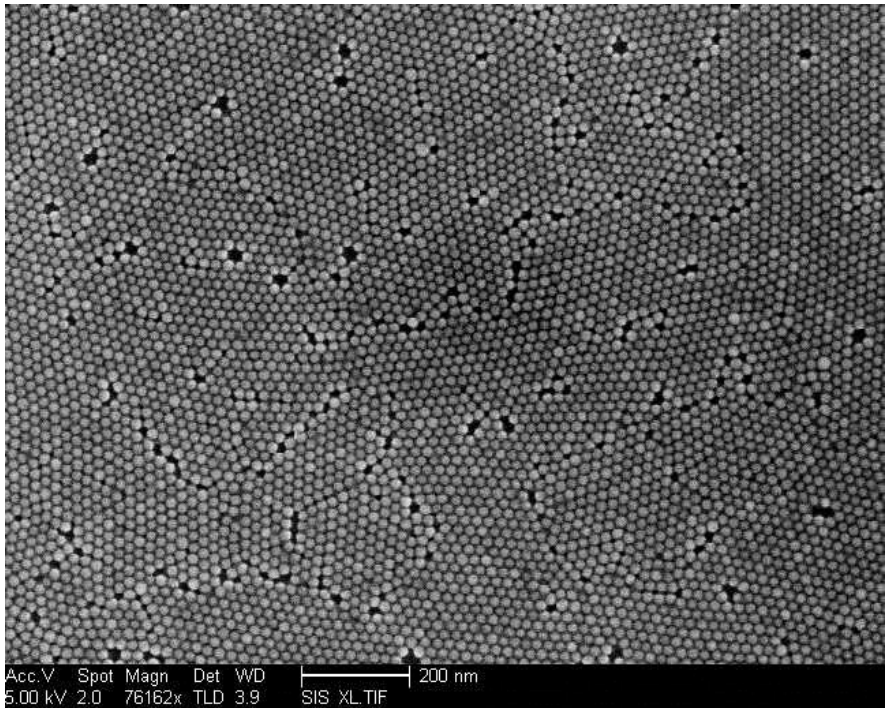




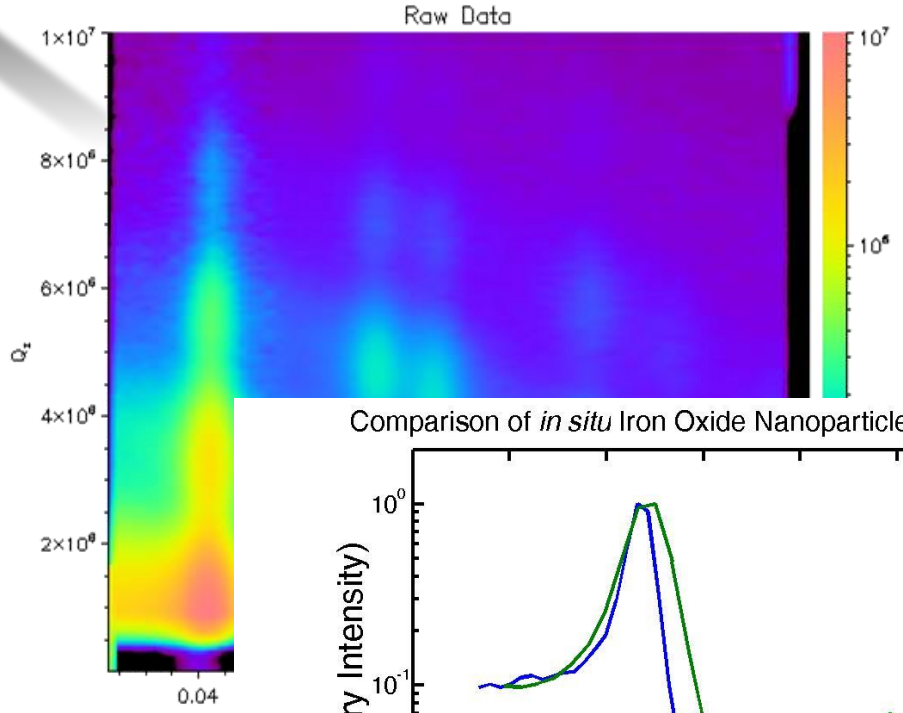
- General Liquid Surface Beamline
- Large Angular Range

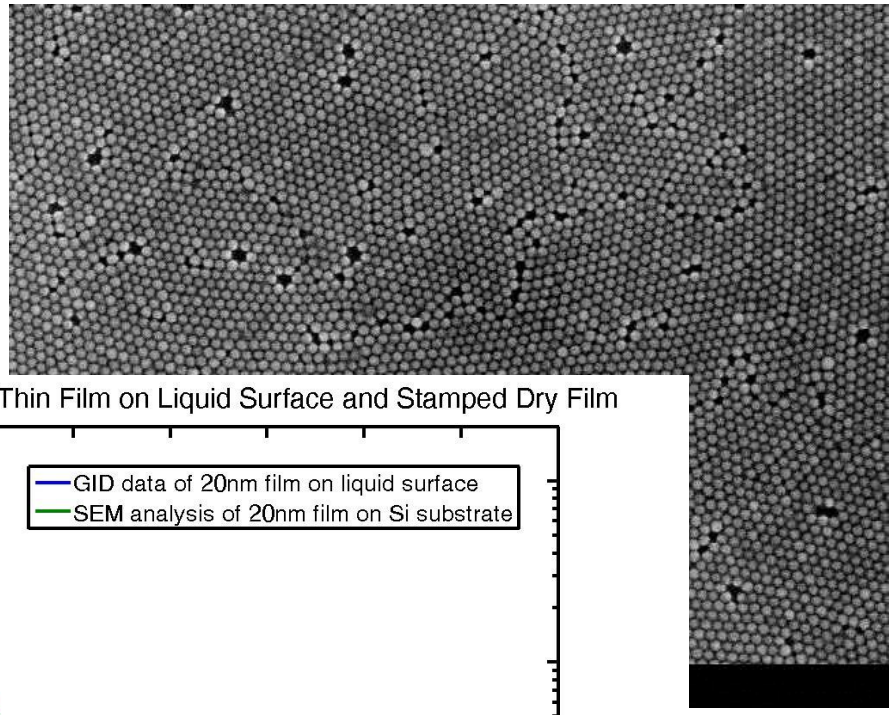
Preservation of Structure



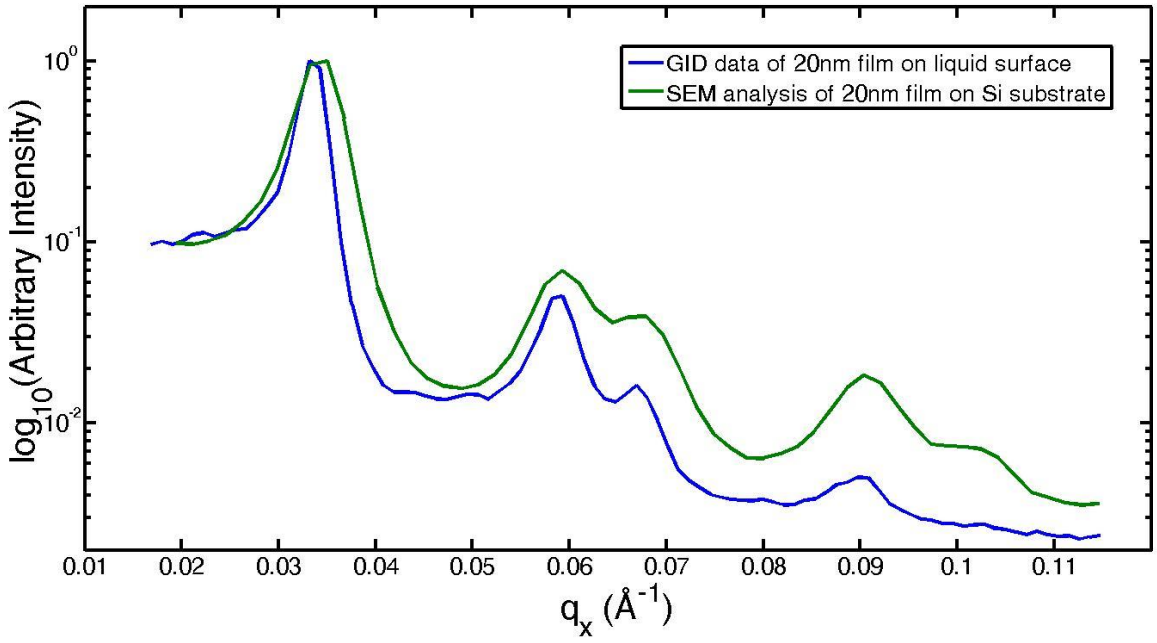


Preservation of Structure

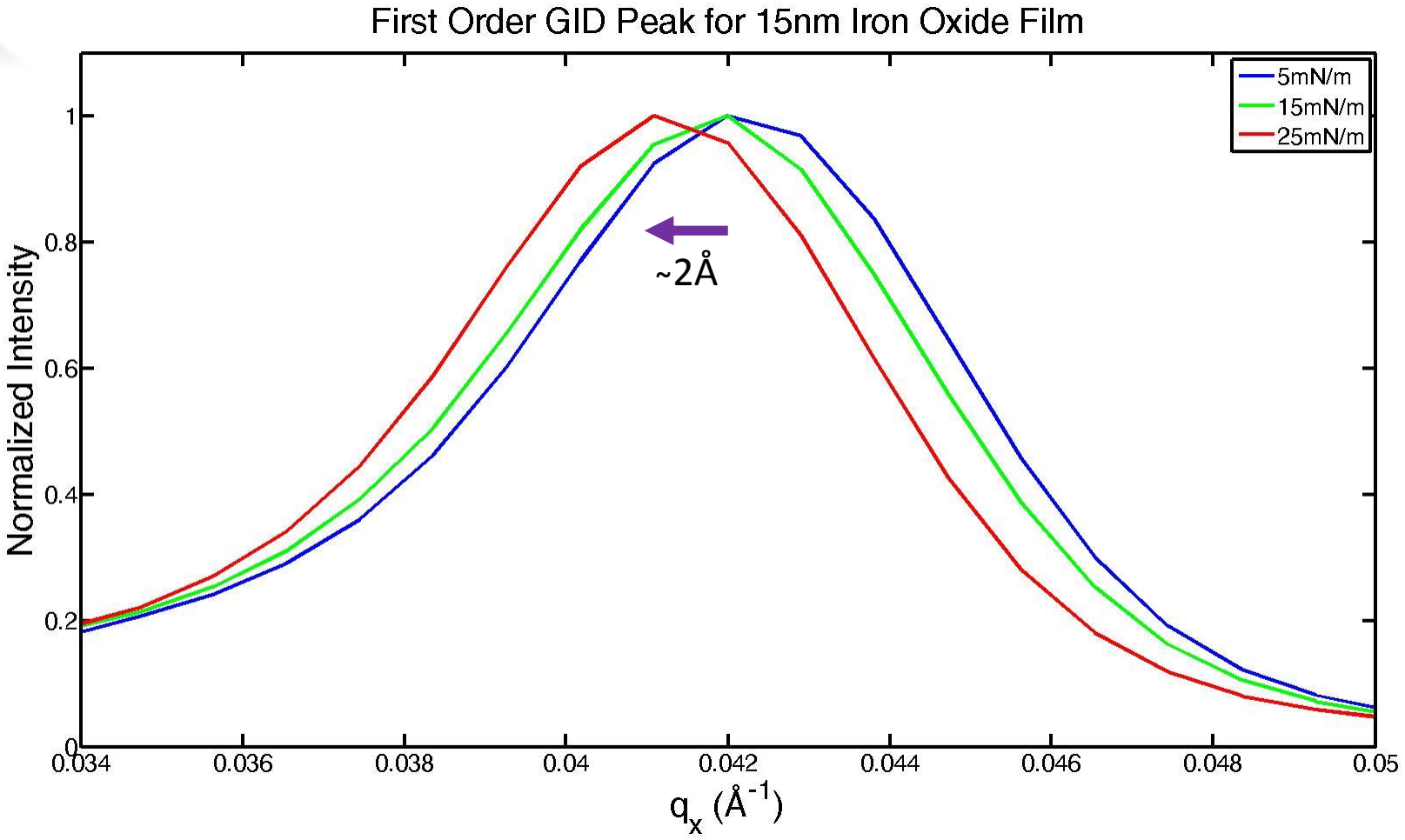




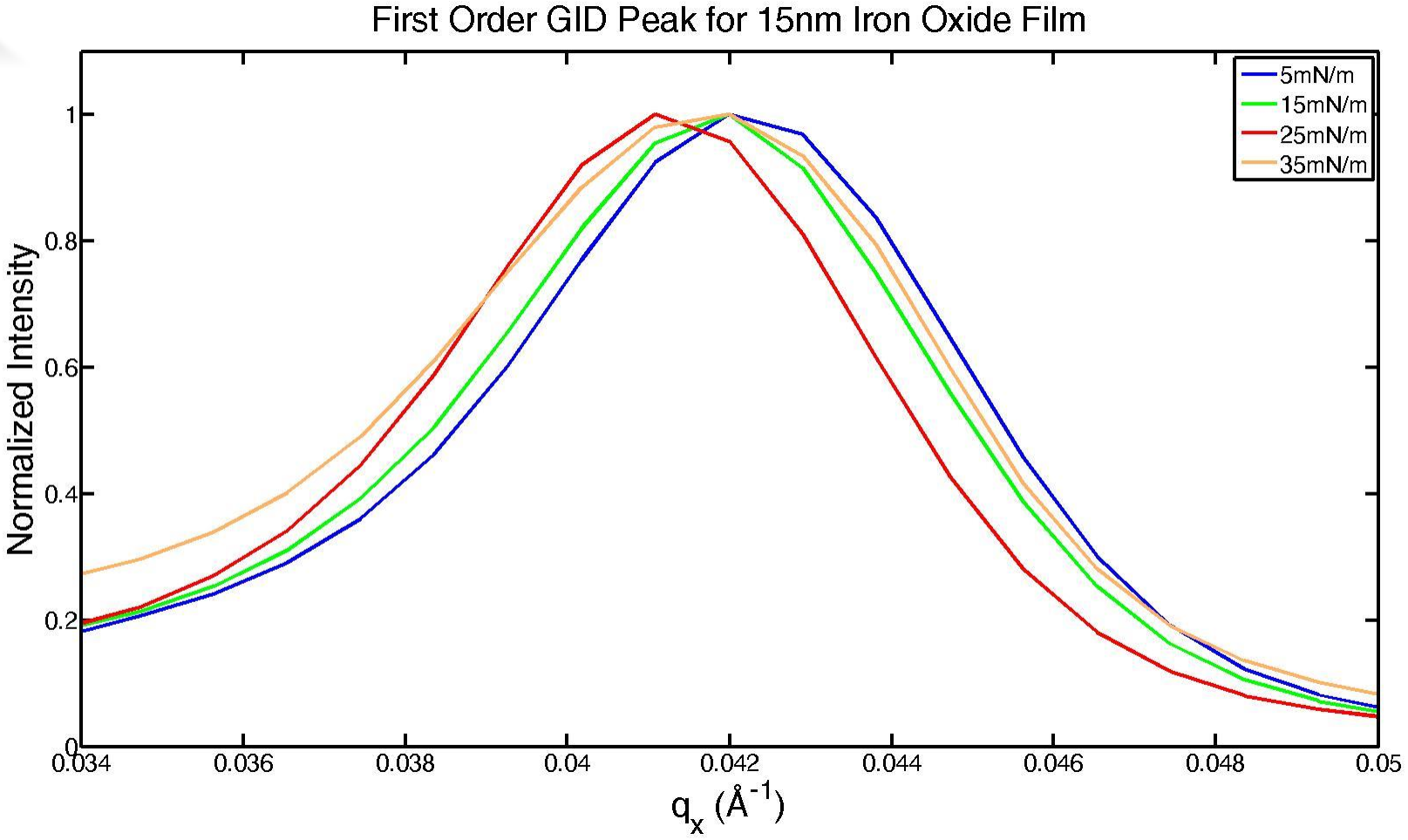
Comparison of *in situ* Iron Oxide Nanoparticle Thin Film on Liquid Surface and Stamped Dry Film



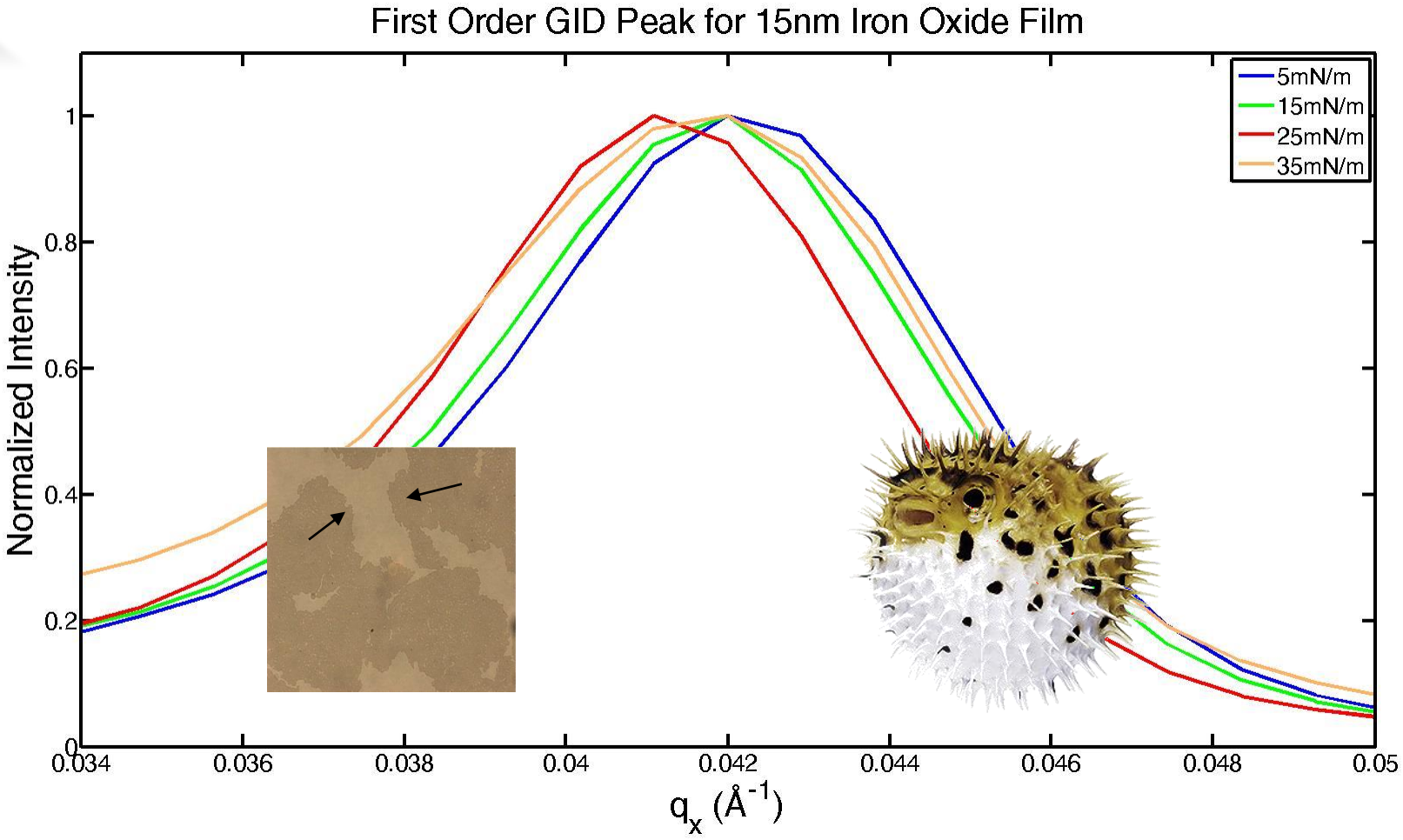
GID During Film Compression



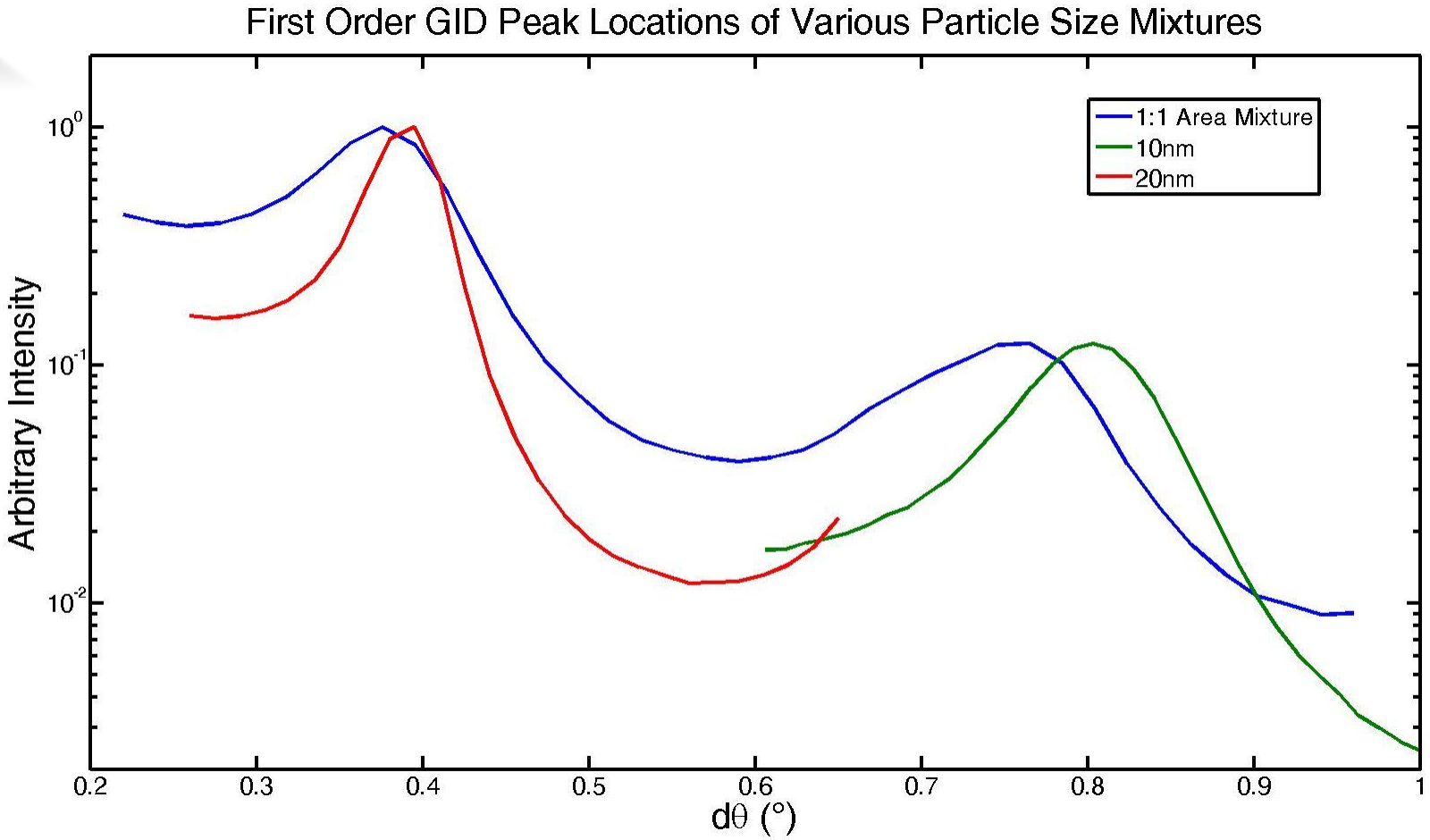
GID During Film Compression



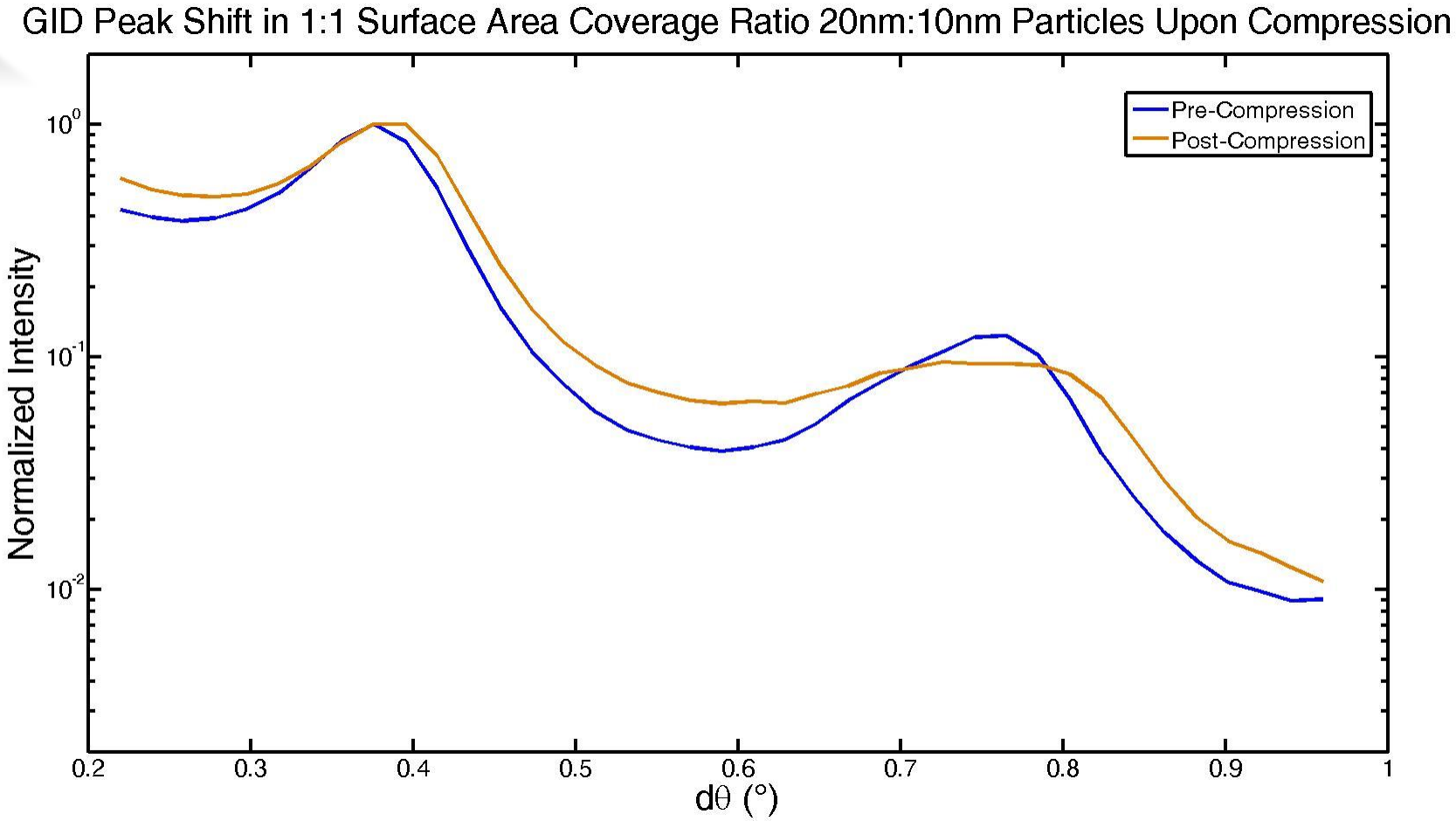
GID During Film Compression



Particle Size Mixtures

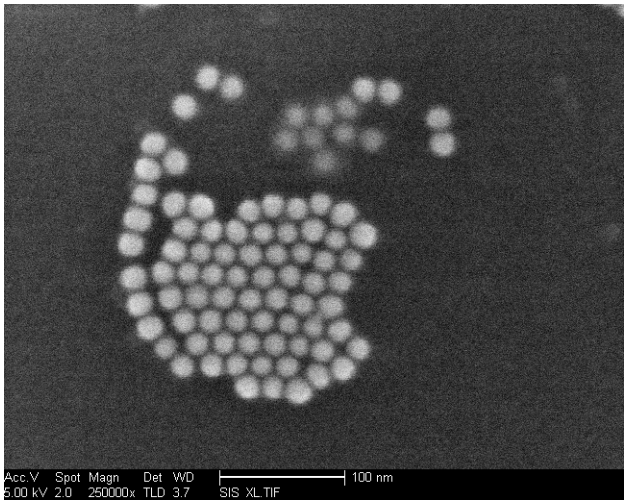


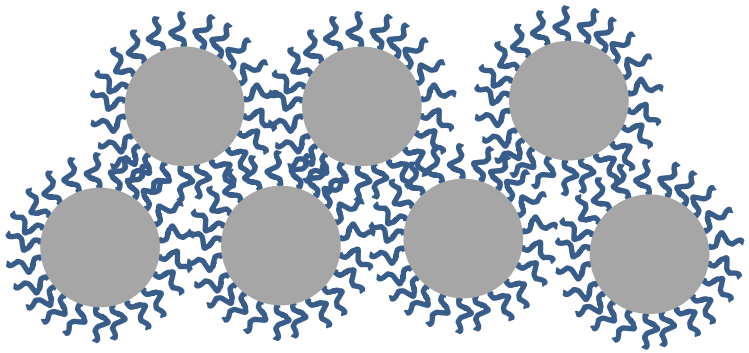
Particle Size Mixtures



Continued Work

- Relate GID Peak Shifts to Particle Dynamics (XPCS)





- How is In-Plane Spacing Affected by Multilayer Formation?

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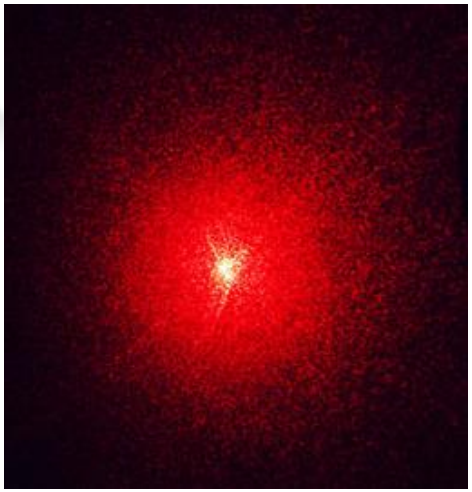
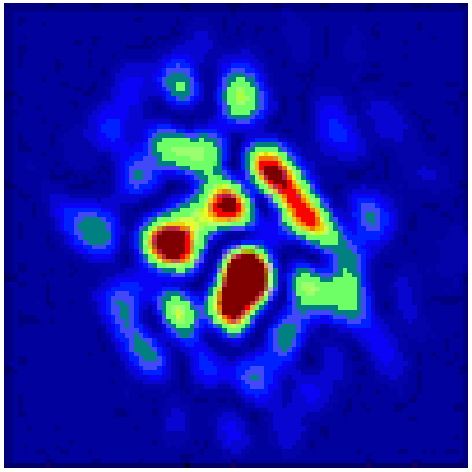
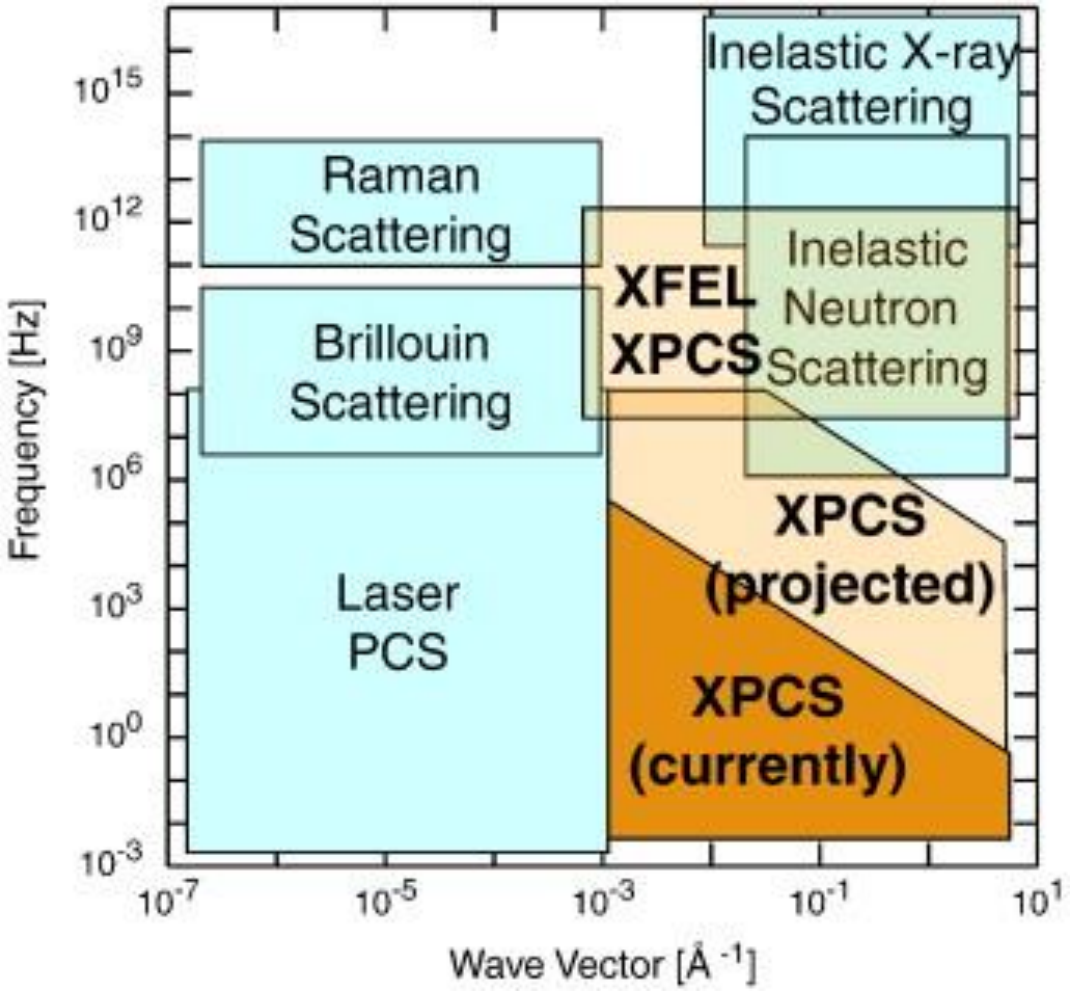
Coherent Speckle





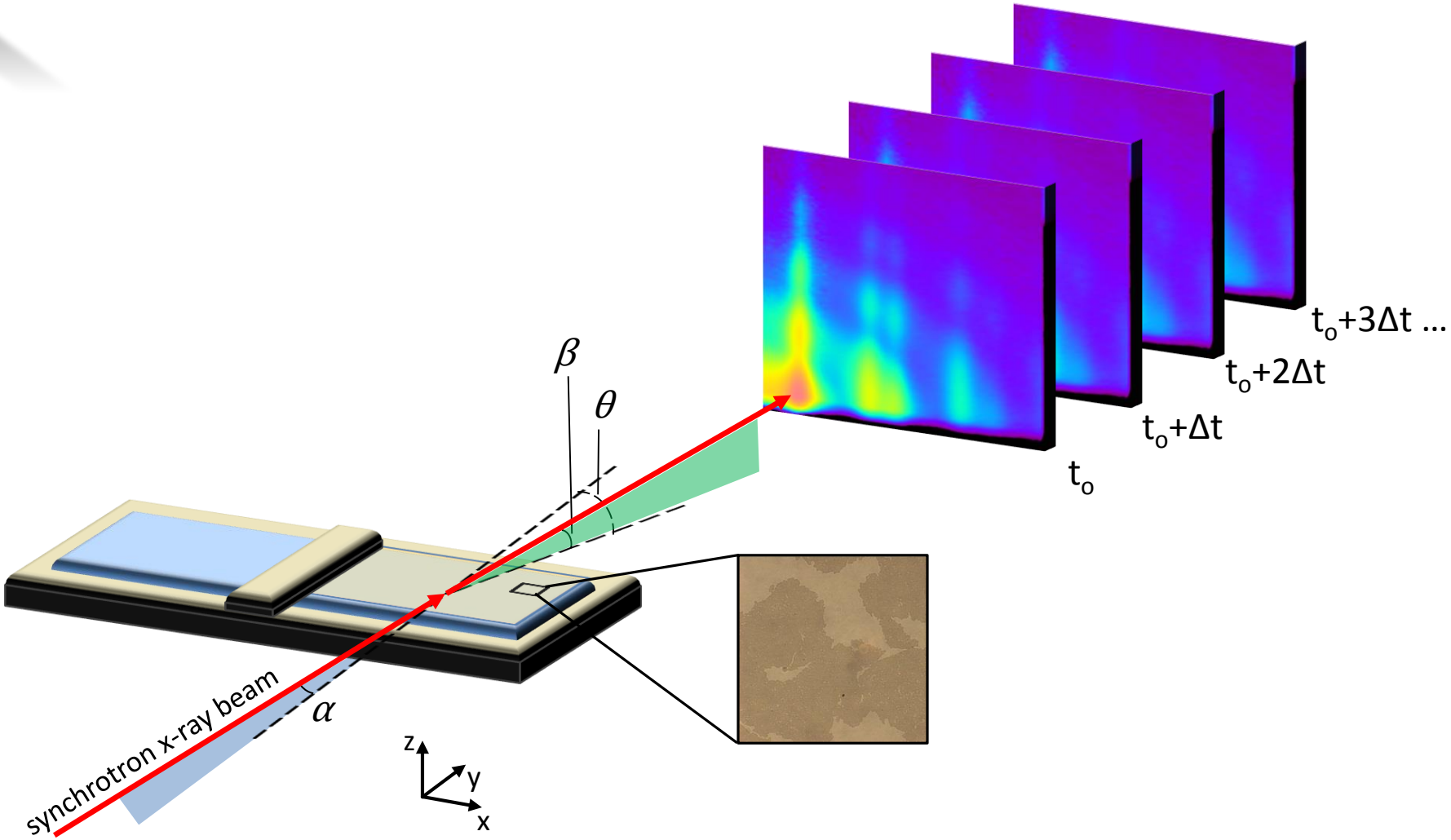


Leheny, R.L. (2012). *Current Opinion in Colloid & Interface Science*, *17*(1)

~~Dynamic Light Scattering~~

- Wrong Length Scale
- Difficult to Couple

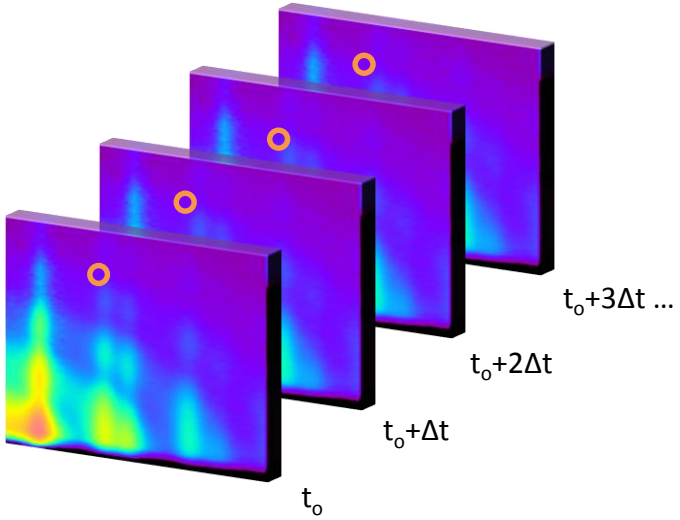
X-Ray Photon Correlation Spectroscopy (XPCS)

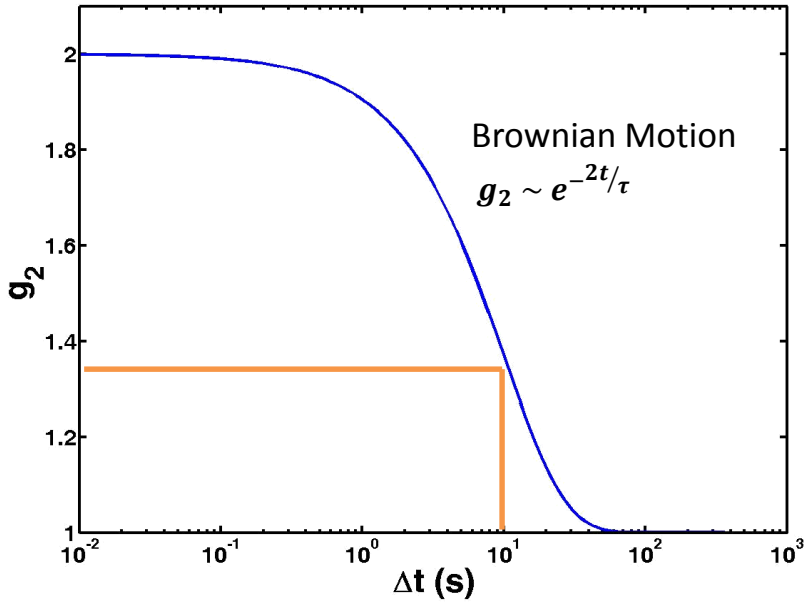


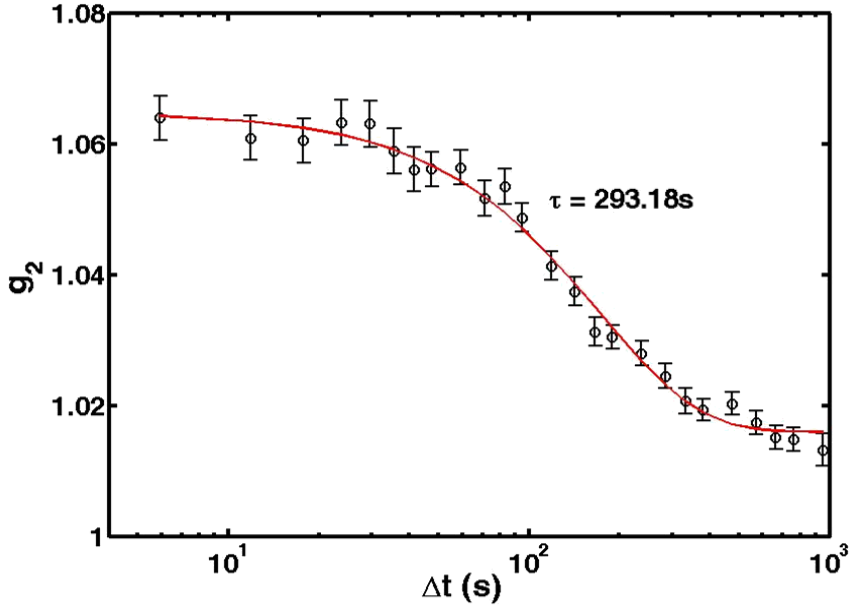
Interparticle Dynamics

$$g_2(\Delta t) = \frac{\langle I(t)I(t+\Delta t)\rangle_t}{\langle I(t)\rangle_t^{\,2}}$$

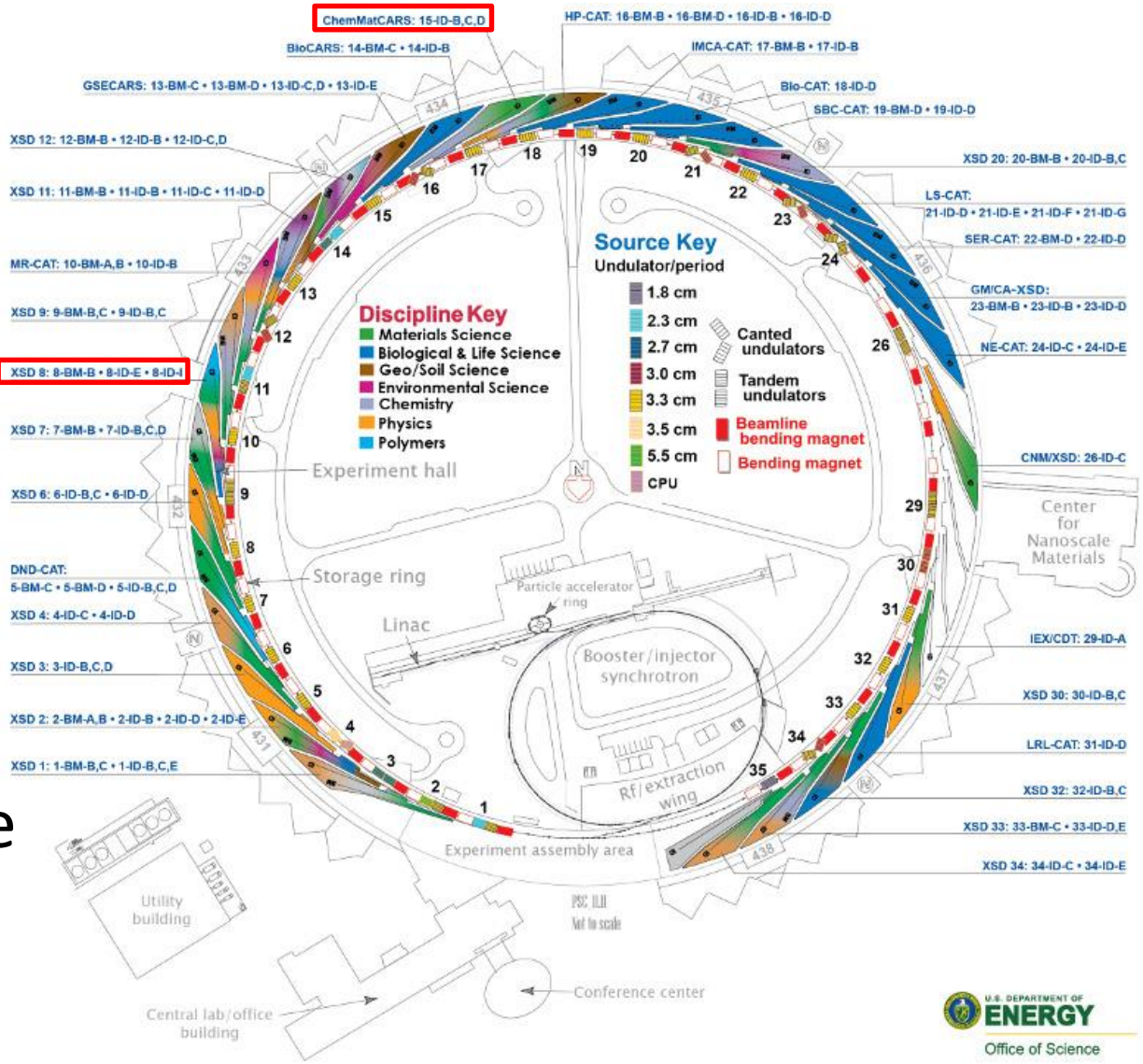
$$g_2(\Delta t) = 1 + \beta[g_1(\Delta t)]^{\,2}$$







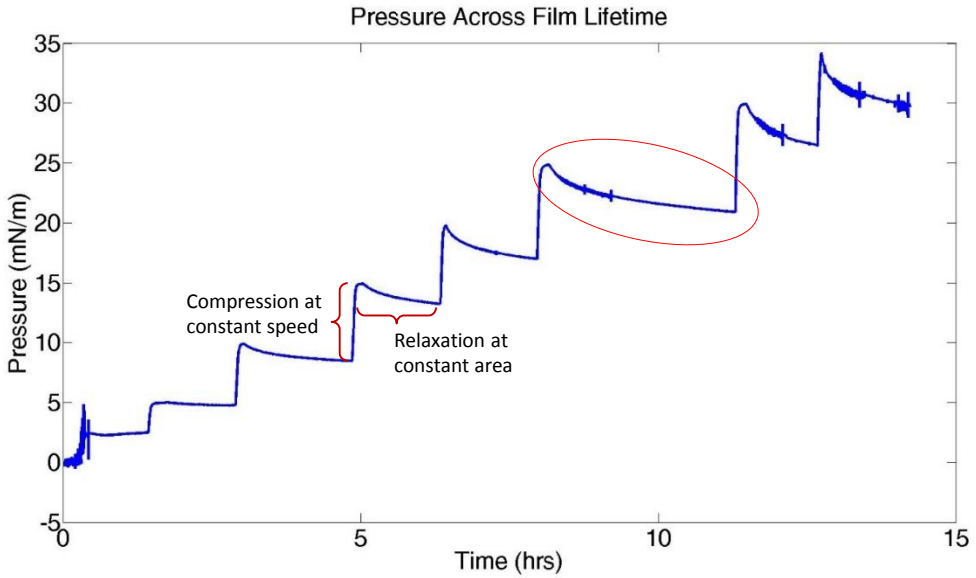
Experimental Location

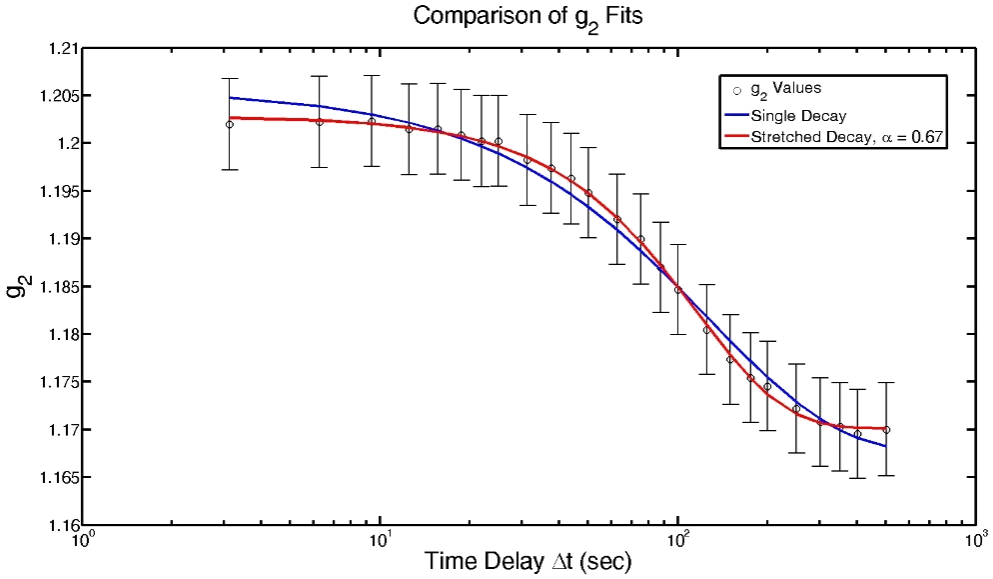


- Beam Coherence
- Better Angular Resolution

Glassy or Jammed State

- Inhomogeneous Dynamics
- Stretched Exponential (Kohlrausch-Williams-Watts)
- Isotherm





Single Exponential (non-glassy) $g_2 \propto e^{-\frac{t}{\tau}}$

Stretched Exponential (glassy) $g_2 \propto e^{-\left(\frac{t}{\tau}\right)^{\alpha}}$

Williams, G., & Watts, D.C. (1970). *Transactions of the Faraday Society*, *66*

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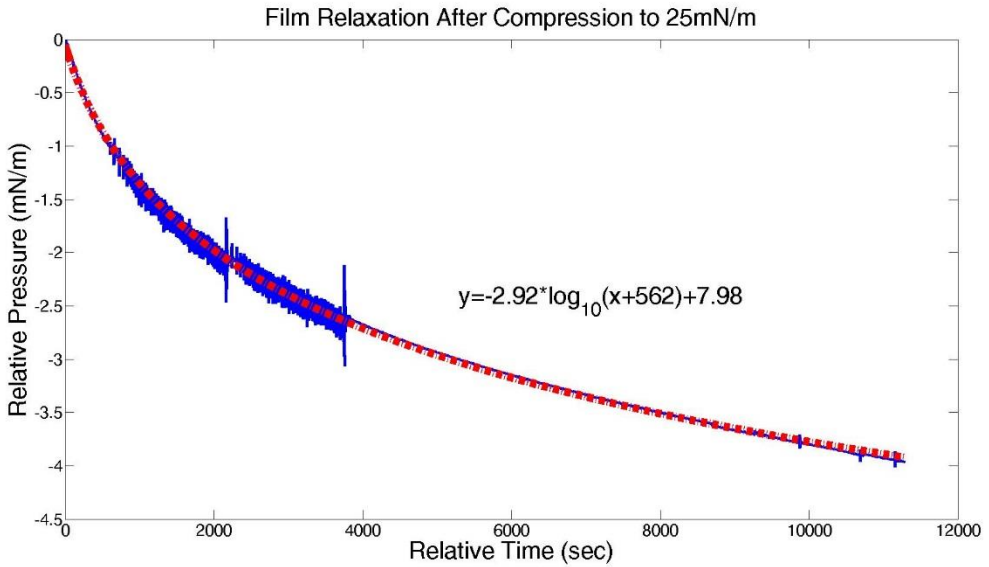

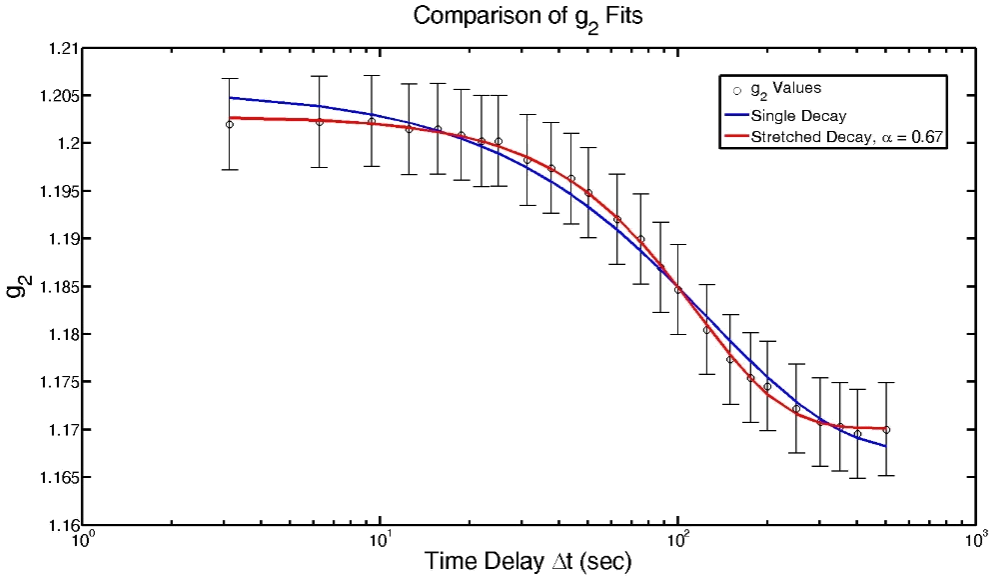

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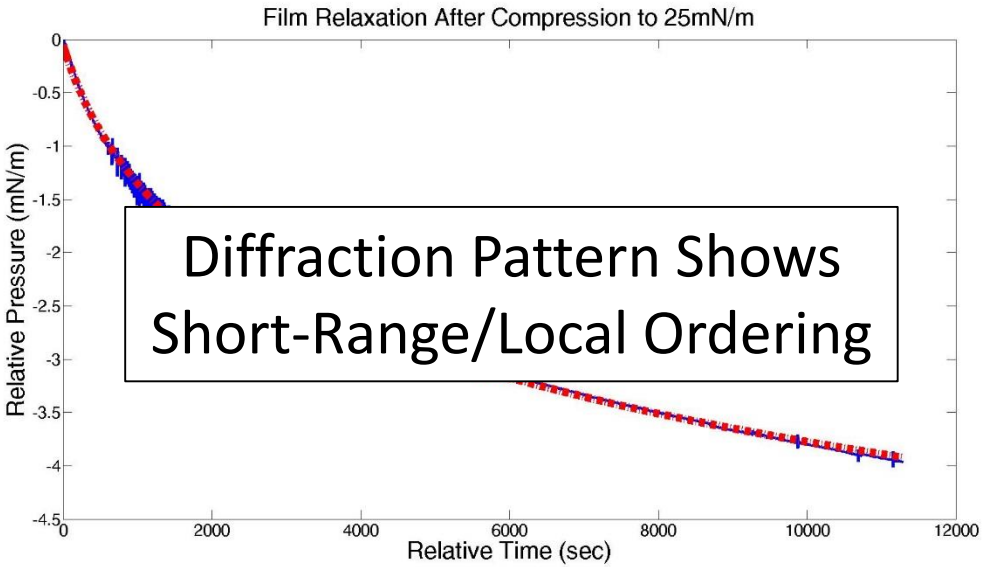
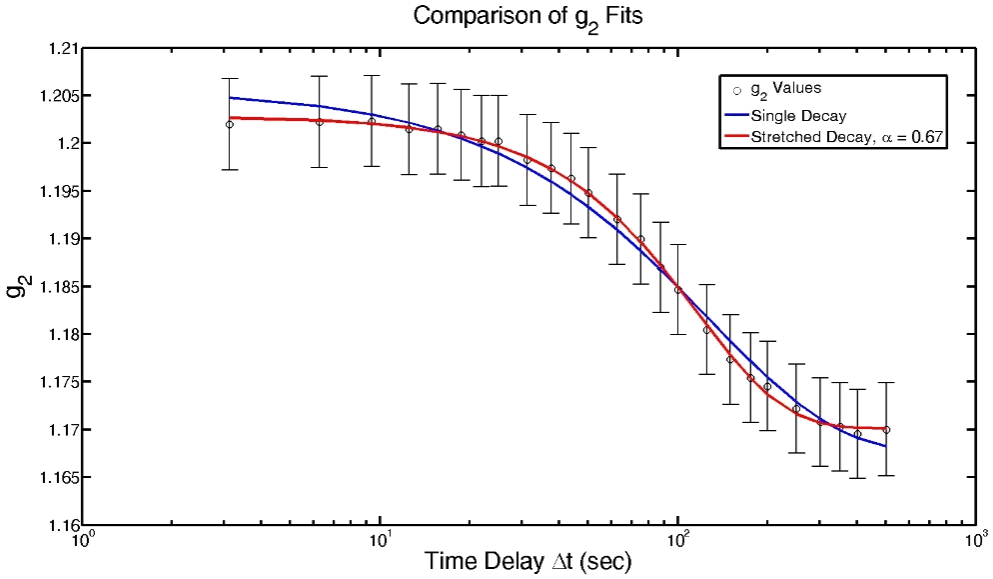


Diffraction Pattern Shows Short-Range/Local Ordering



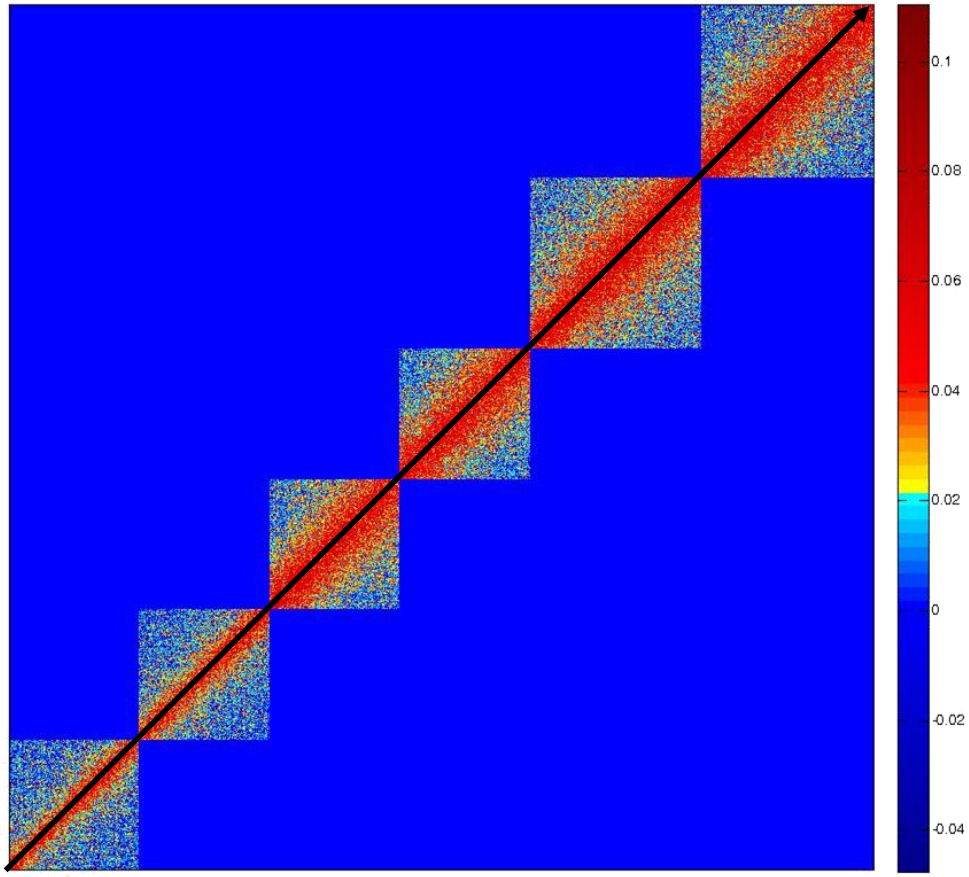
Single Exponential (non-glassy) $g_2 \propto e^{-\frac{t}{\tau}}$

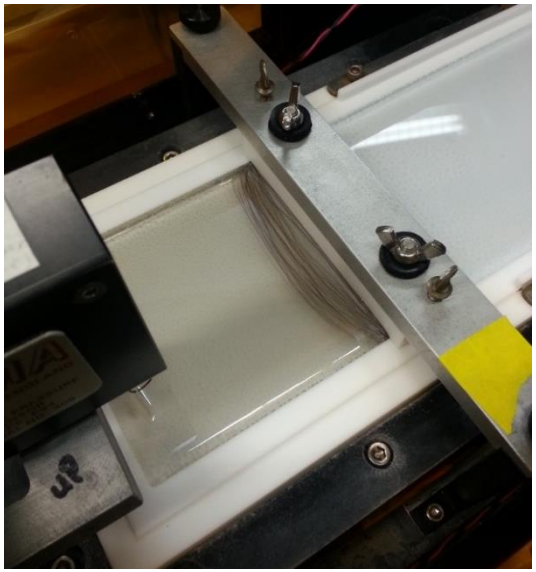
Stretched Exponential (glassy) $g_2 \propto e^{-\left(\frac{t}{\tau}\right)^{\alpha}}$

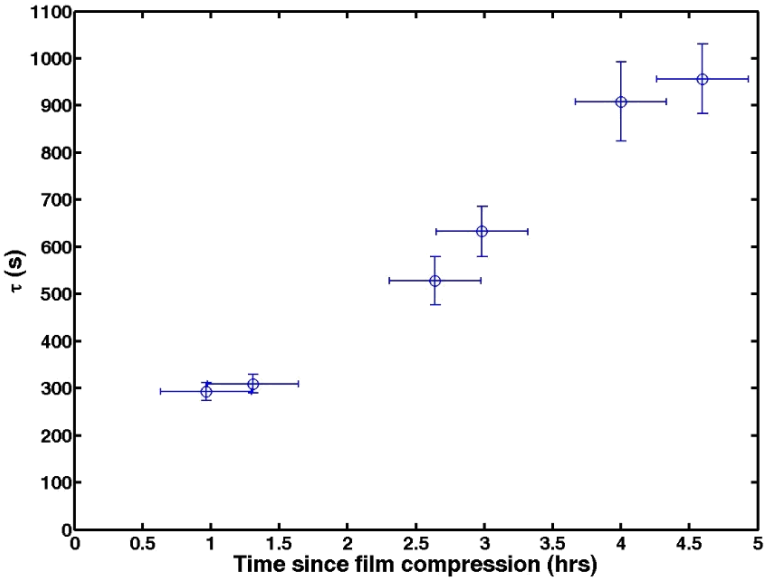
Williams, G., & Watts, D.C. (1970). *Transactions of the Faraday Society*, *66*

Viscoelasticity

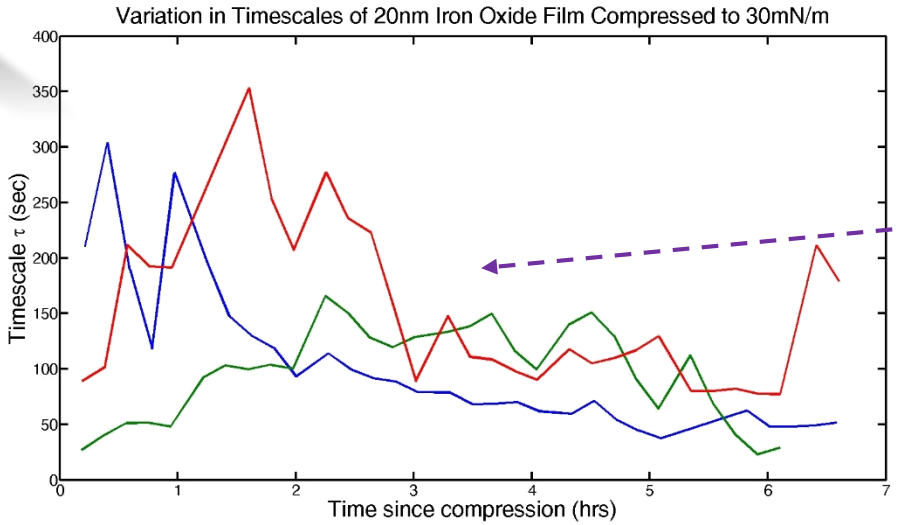
$$g_{2-time}(\Delta t_1, \Delta t_2) = \frac{\langle I(t+\Delta t_1) I(t+\Delta t_2)\rangle_t}{\langle I(t)\rangle^2}$$





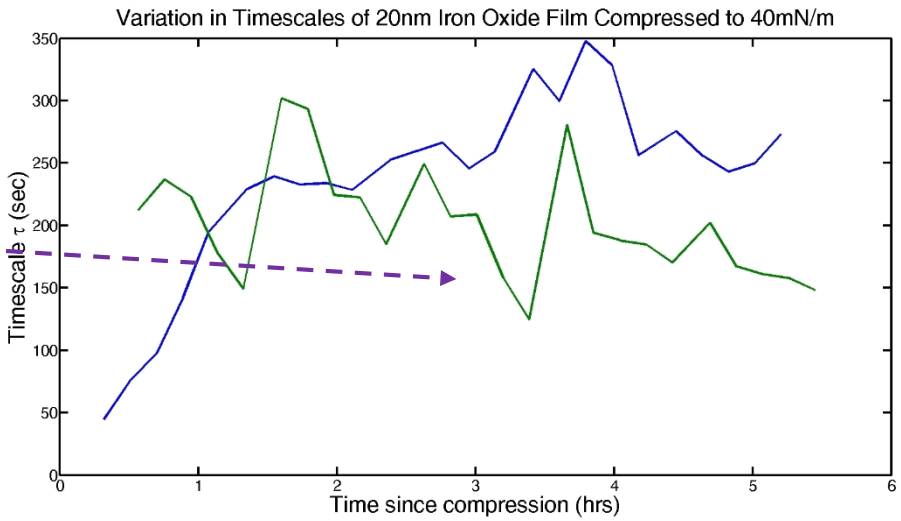


Timescale-Pressure Dependence



$\bar{\tau}_{30mN/m} = 120s$

$\bar{\tau}_{40mN/m} = 220s$




SEMINAR ADVANCEMENT
B I N G O
Speaker bashes previous work
Repeated use of "um…"
Speaker sucks up to host professor
Host Professor falls asleep
Speaker wastes 5 minutes explaining outline
Laptop malfunction
Work ties in to Cancer/HIV or War on Terror
"…et al."
You're the only one in your lab that bothered to show up
Entire slide filled with equations
Blatant typo
"The data *clearly* shows…"
FREE
Speaker runs out of time
Use of Powerpoint template with blue background
References Advisor (past or present)
There's a Grad Student wearing same clothes as yesterday
Bitter Post-doc asks question
"That's an interesting question"
"Beyond the scope of this work"
Professor bobs head fighting sleep
Speaker forgets to thank collaborators
Cell phone goes off
Results conveniently show improvement
"Future work will…"
You've no idea what's going on
JORGE CHAM © 2007

Jacob

Q-Dependence of Timescale

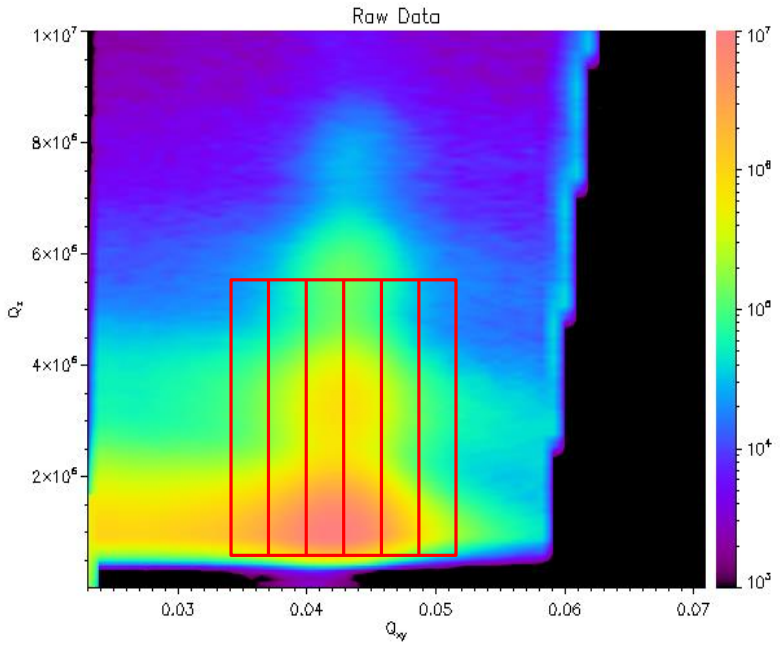
Brownian Motion

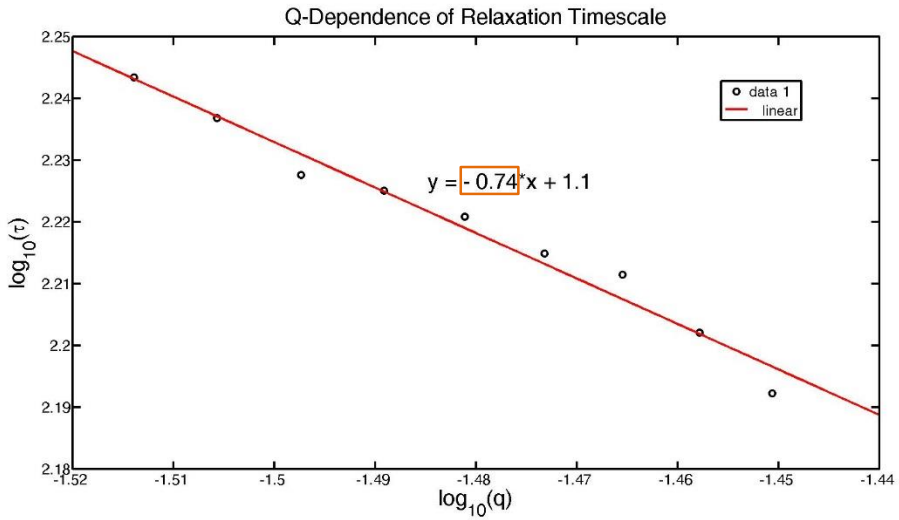
$$\langle x^2 \rangle = 2Dt$$

$$\langle x^2 \rangle = \left(\frac{2\pi}{q}\right)^2 \qquad t = \tau$$

$$\tau = \frac{2\pi^2}{q^2 D}$$

$$\ln \tau = -2 \ln q + C$$





Q-Dependence of Timescale

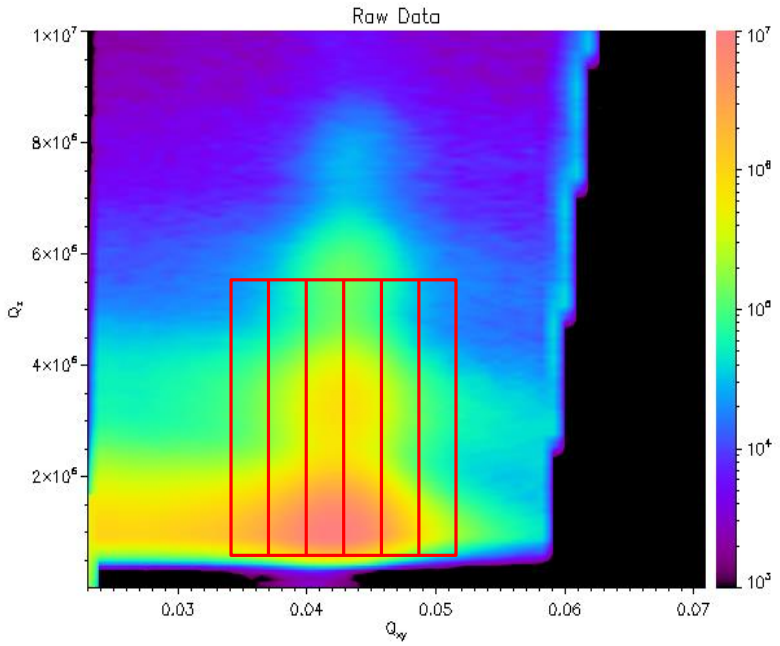
Non-Brownian Motion

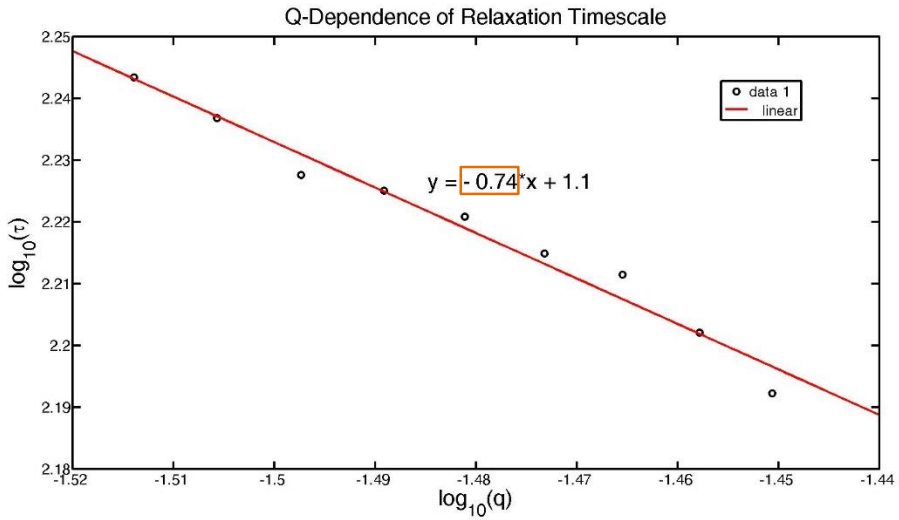
$$\langle x^2 \rangle = 2Dt^{n}$$

$$\langle x^2 \rangle = \left(\frac{2\pi}{q}\right)^2 \qquad t = \tau$$

$$\tau = \frac{2\pi^2}{q^2 D}$$

$$\ln \tau = -\frac{2}{n} \ln q + C$$





To Be Continued…

- Framework for Stretched Exponential + Anomalous Diffusion
- Order in Glassy Systems
- Hydrodynamic Interactions

$$H(q) \equiv \frac{D_{\varepsilon}(q)S(q)}{D_0}$$

Kurchan, J., & Levine, D. (2011). *Journal of Physics A*, 44.

Outline

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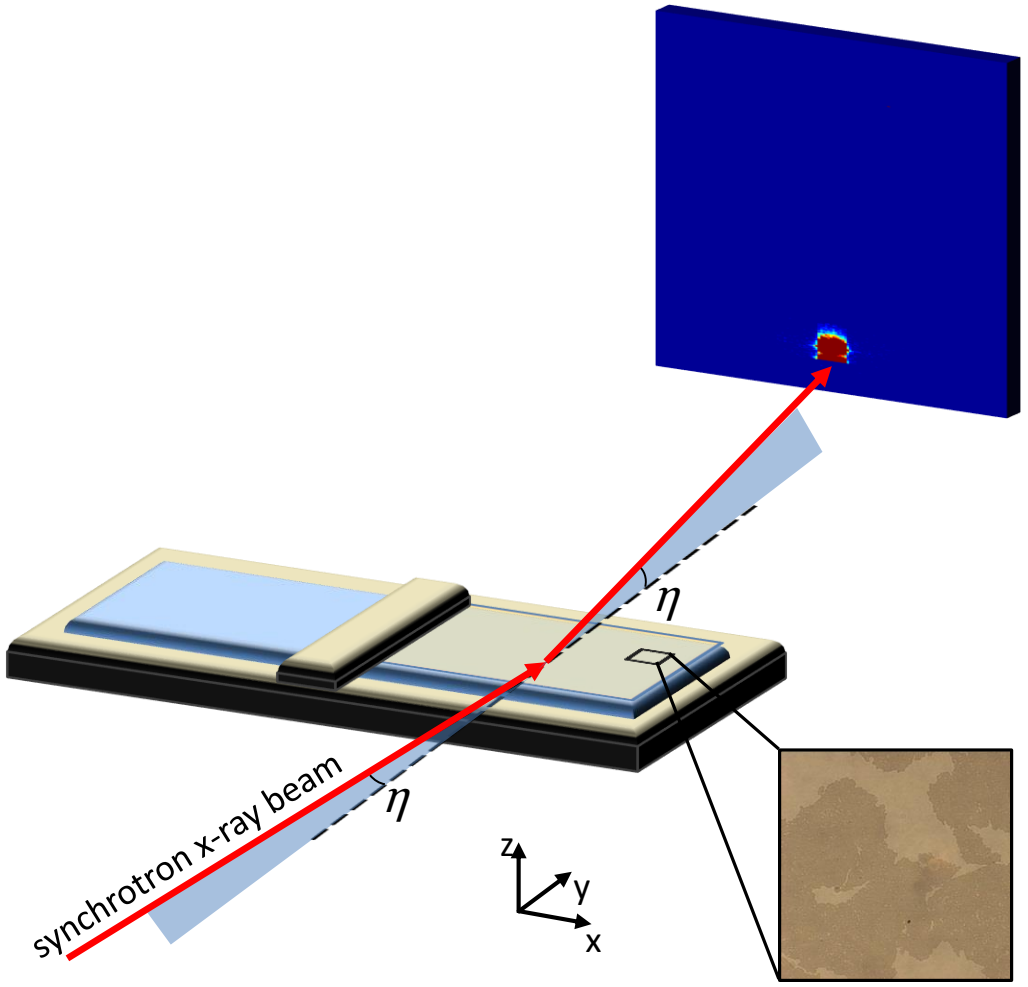
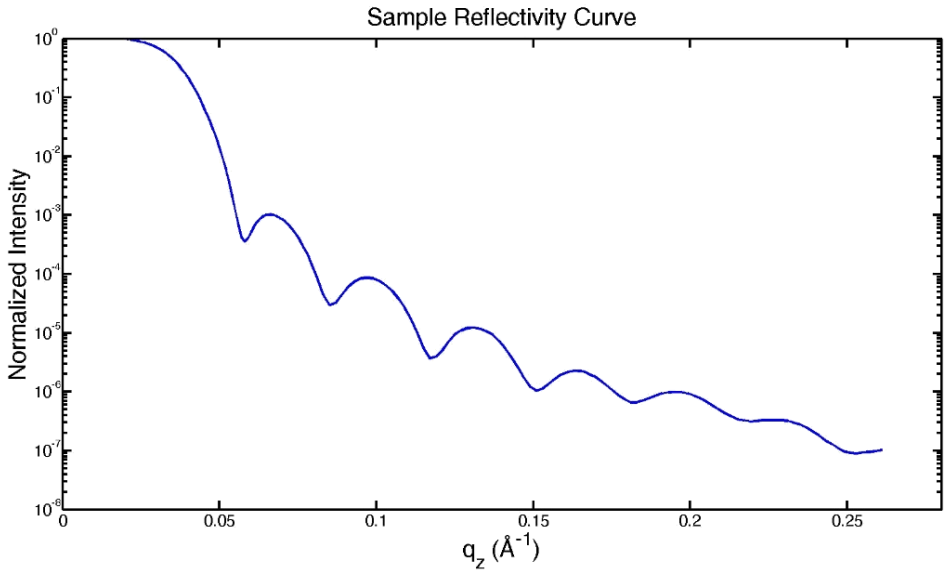
  - Magnetic Effects
  - X-Ray Coherent Diffractive Imaging (CXDI)

X-Ray Reflectivity (XR)



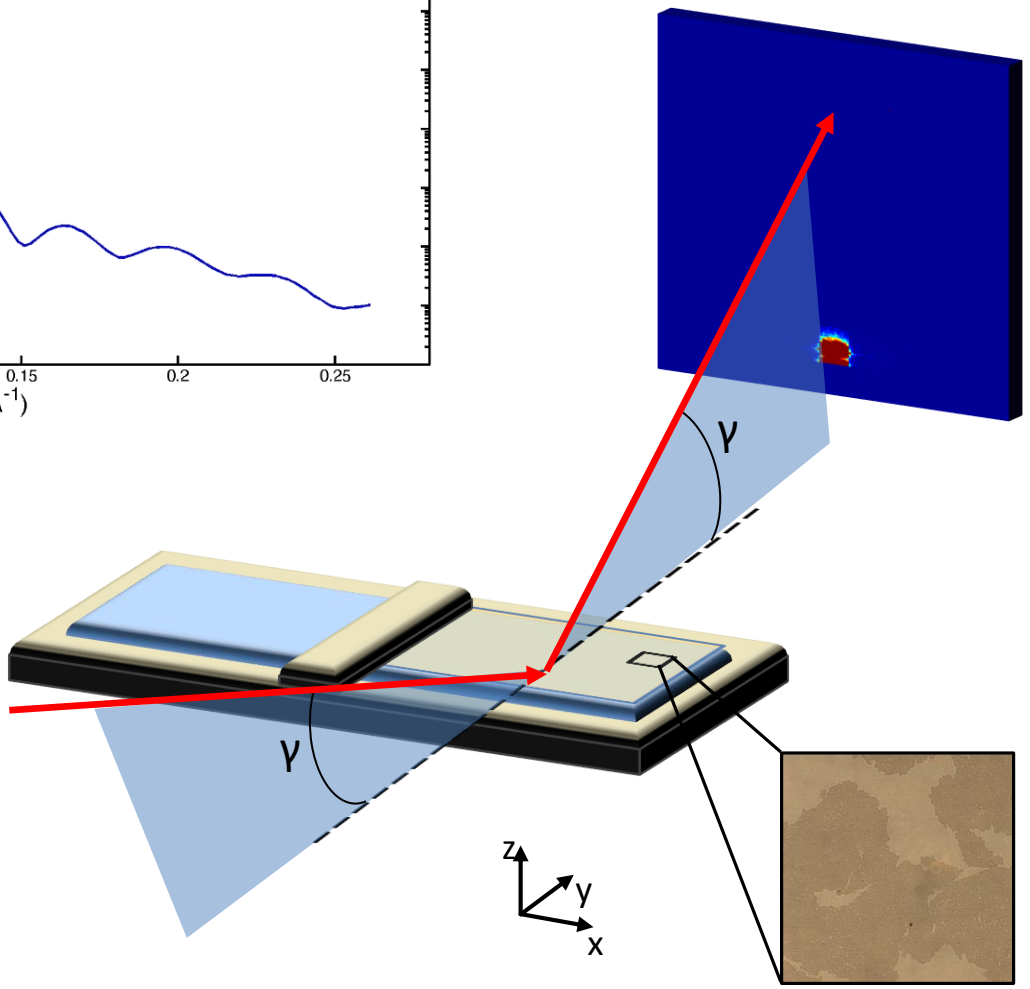
X-Ray Reflectivity (XR)



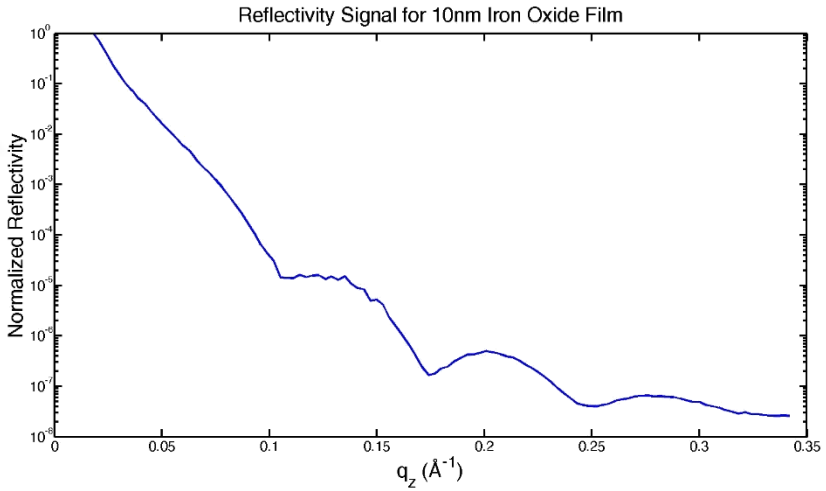
Fresnel Reflectivity

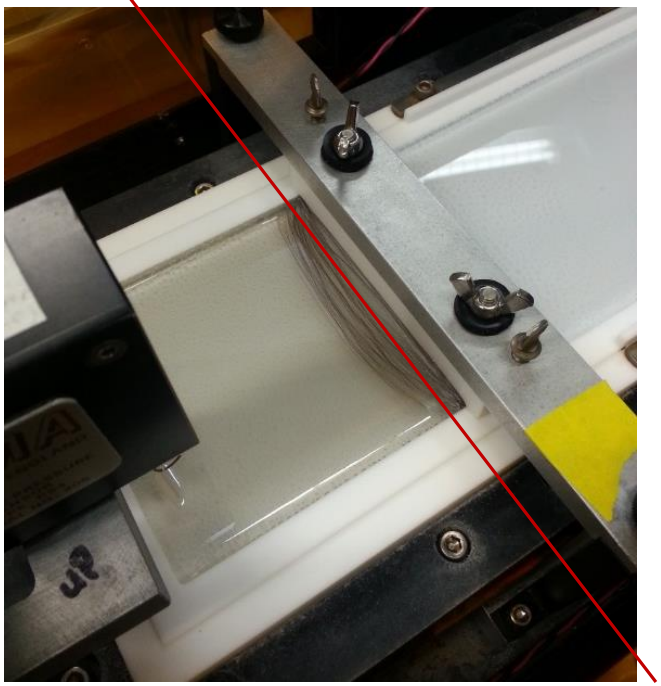
$$R(q_z) \approx \left(\frac{q_c}{2q_z}\right)^4 \left|\int_{-\infty}^{\infty} e^{iq_z z} \frac{d\rho}{dz} dz\right|^2$$

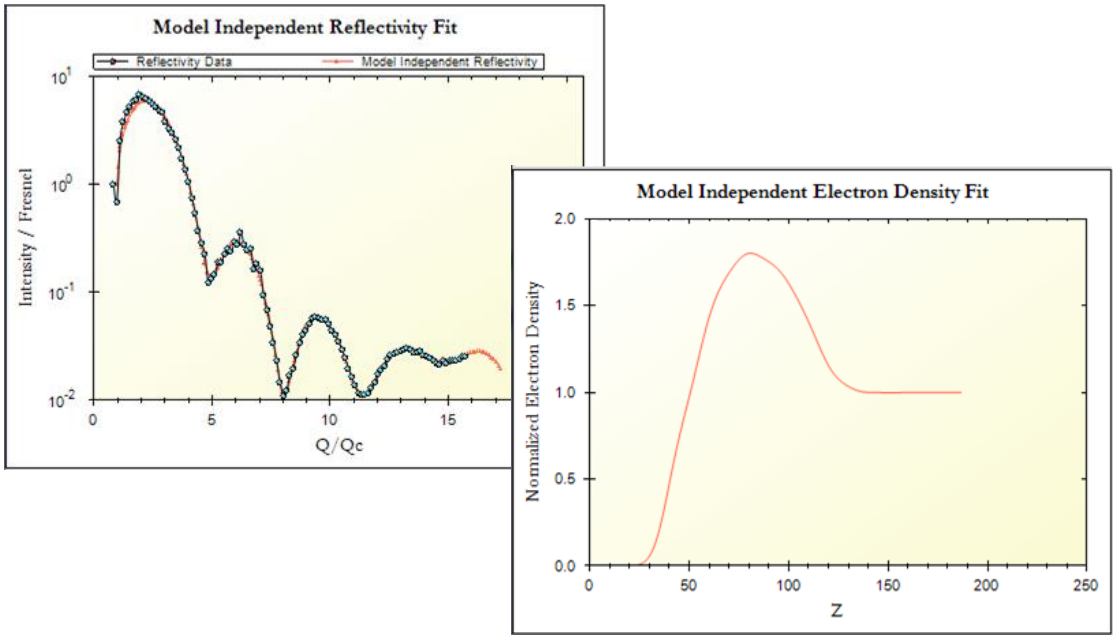
Surface Structure Factor



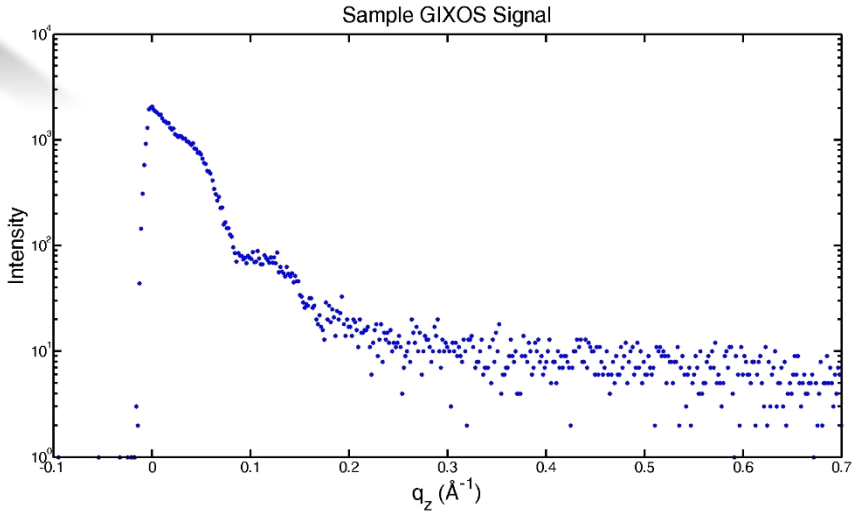
Reflectivity Analysis





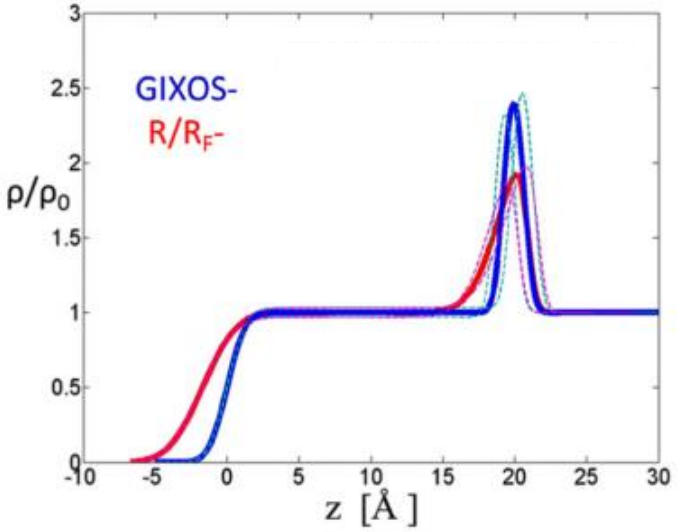


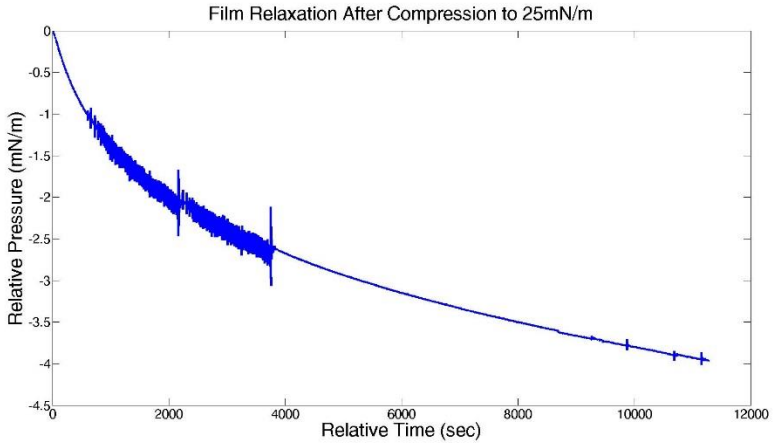
Grazing Incidence X-Ray Off-Specular (GIXOS)



Advantages of GIXOS

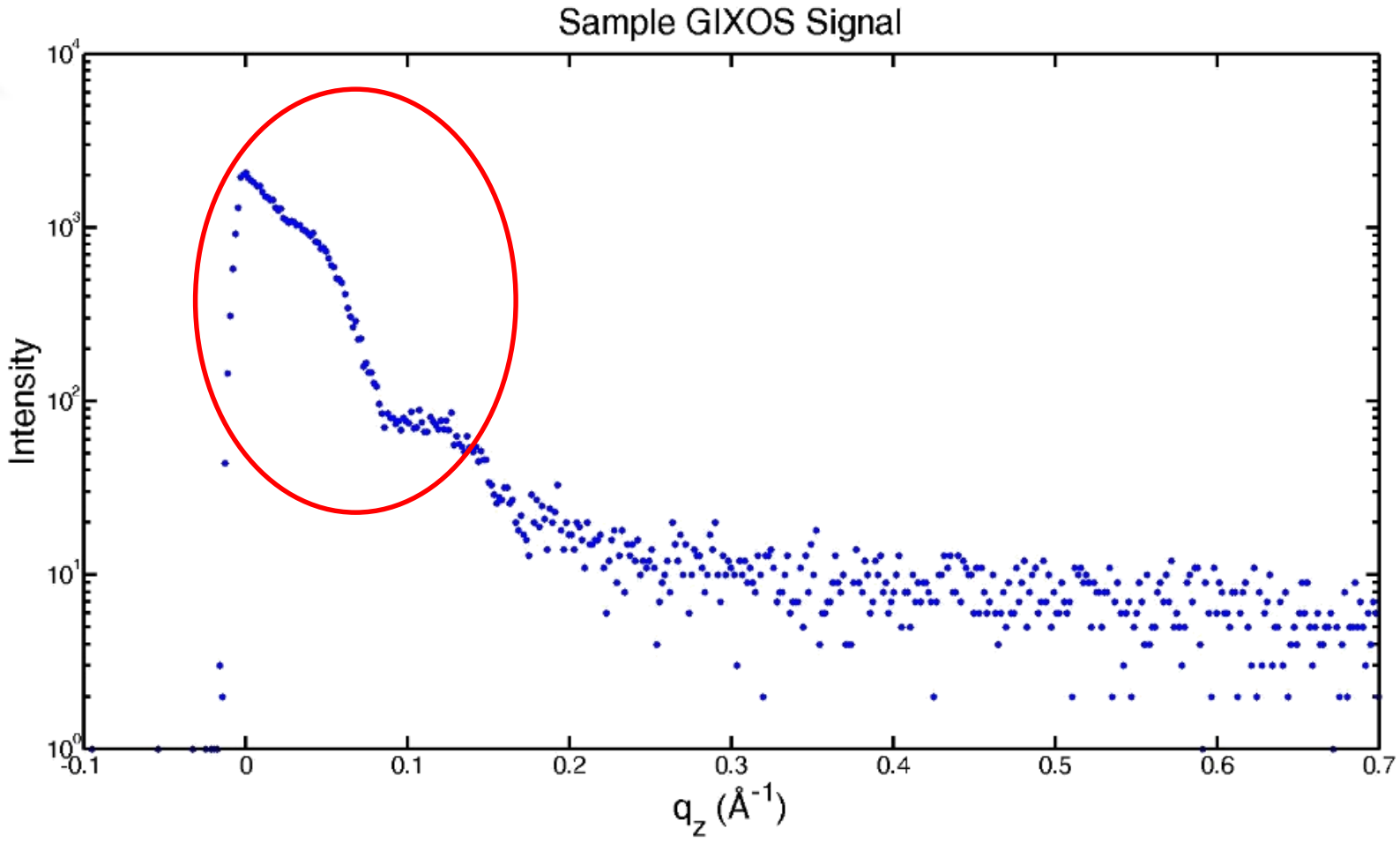
- Faster Data Collection
- Less Sample Damage
- No Sample Motion Required
- Static X-Ray Footprint



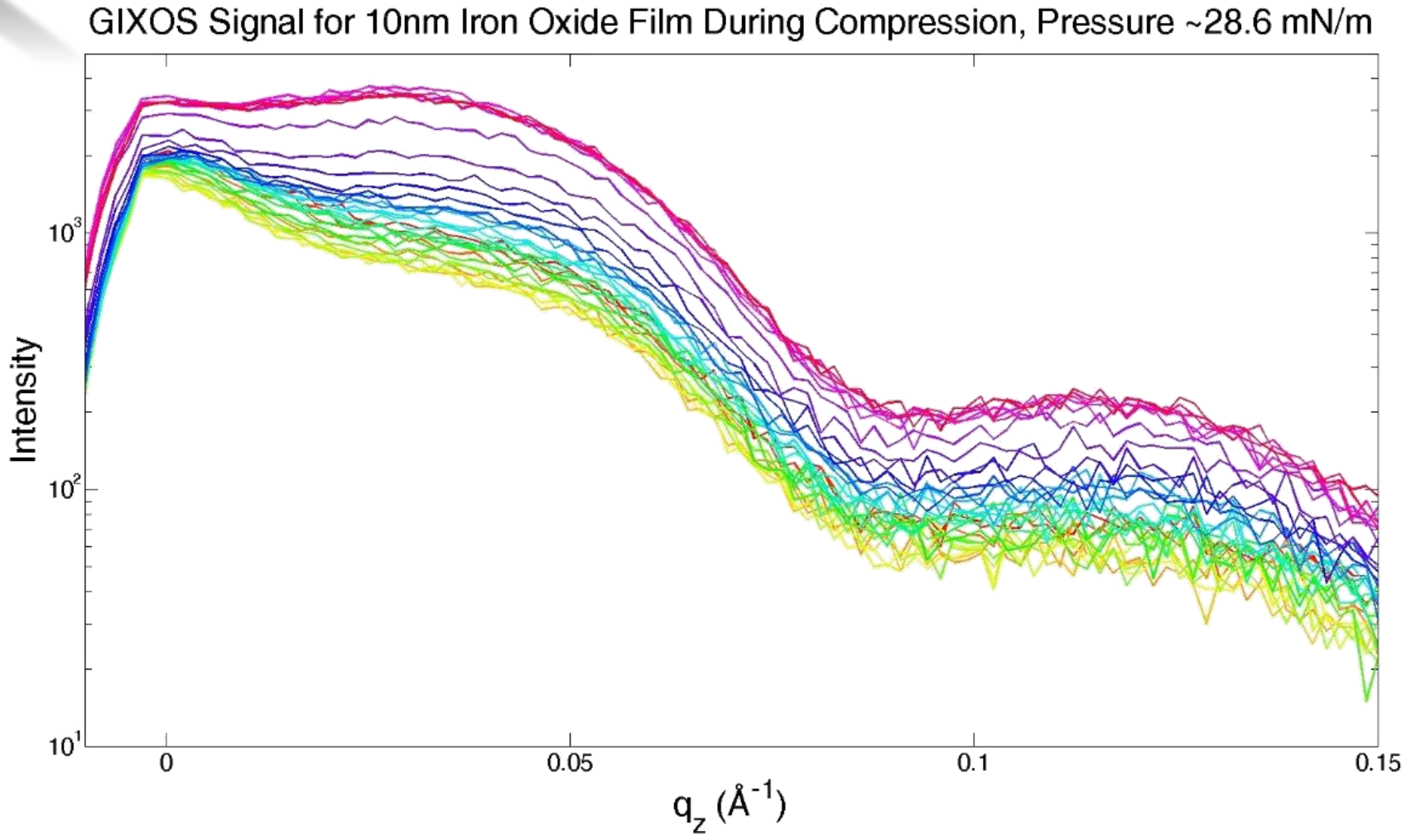


Dai, Y., *et. al.* (2011). *Journal of Applied Physics* , 110.

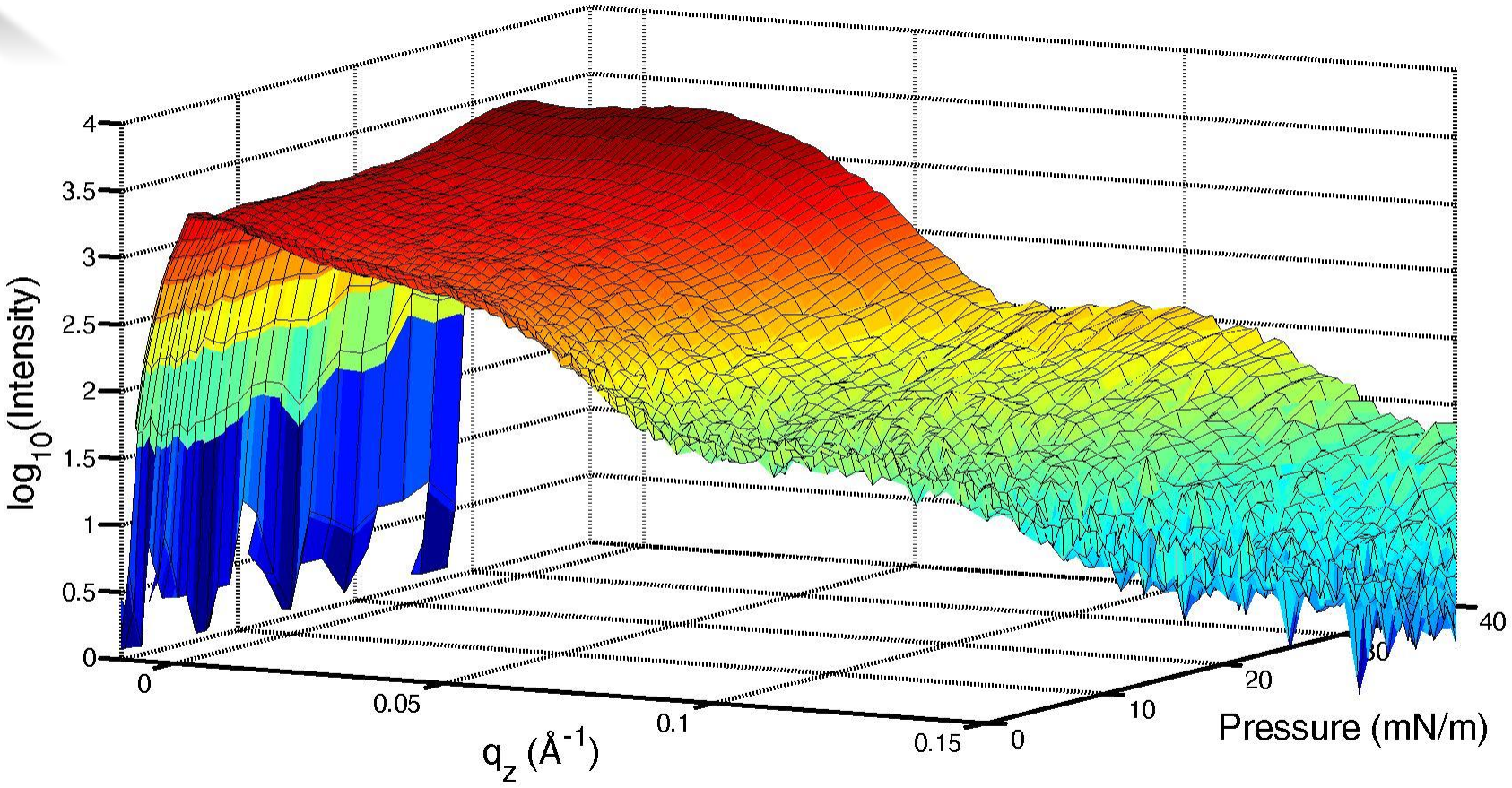
GIXOS During Compression



GIXOS During Compression

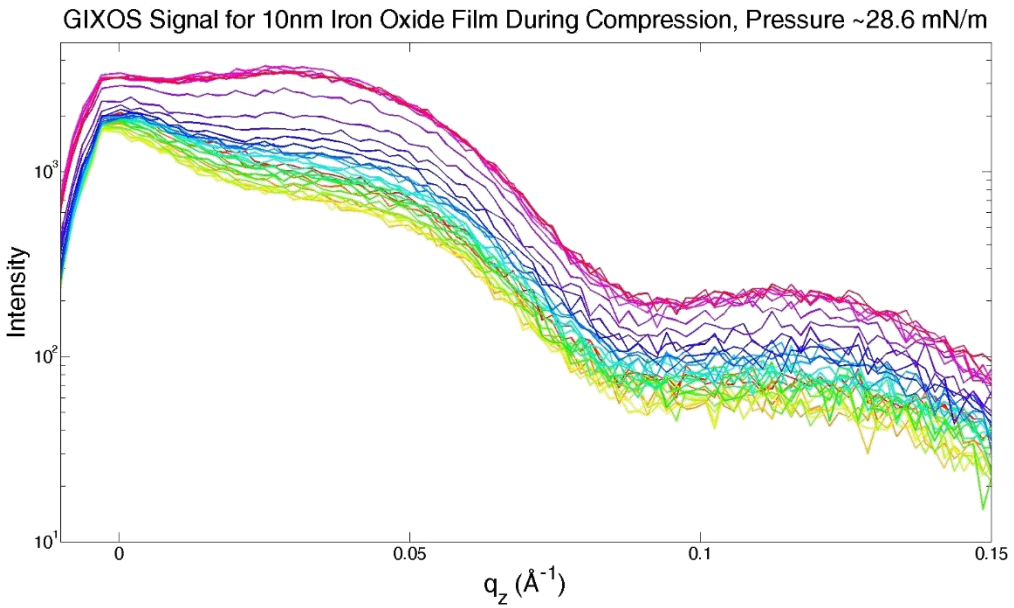


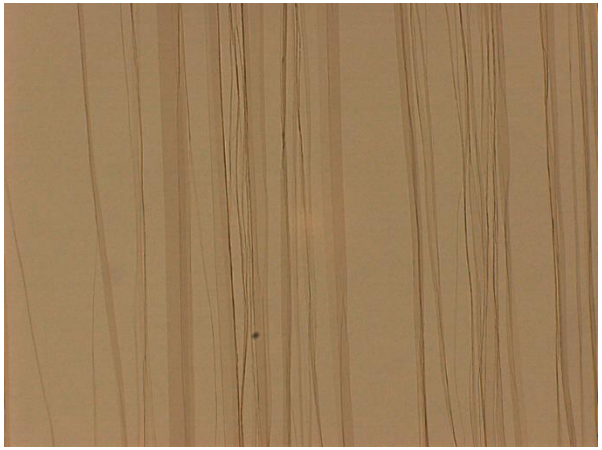
GIXOS During Compression



Continued Work

- Analyze GIXOS Data
- Correlate Intensity Drop with GID Signal





- Effect of Compression Speed on Multilayer Formation

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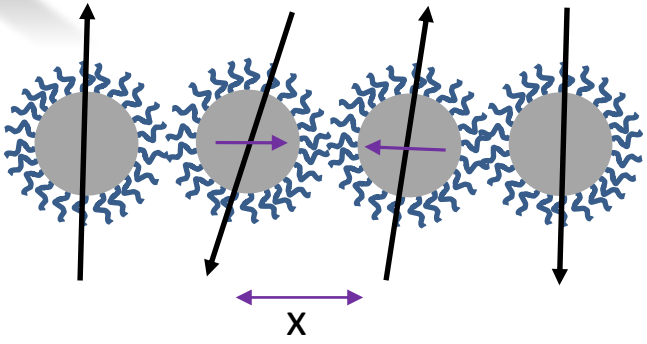
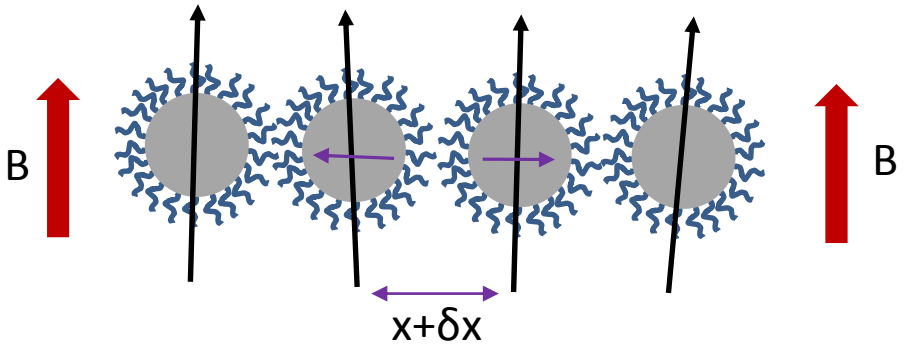
Magnetic Field Application

No External Field

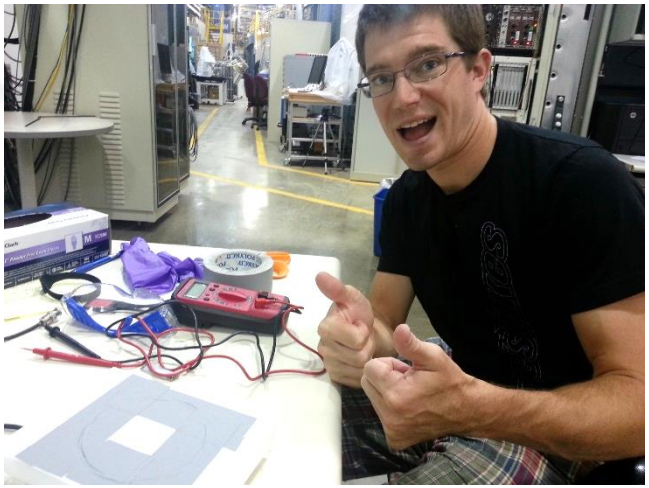


External Field

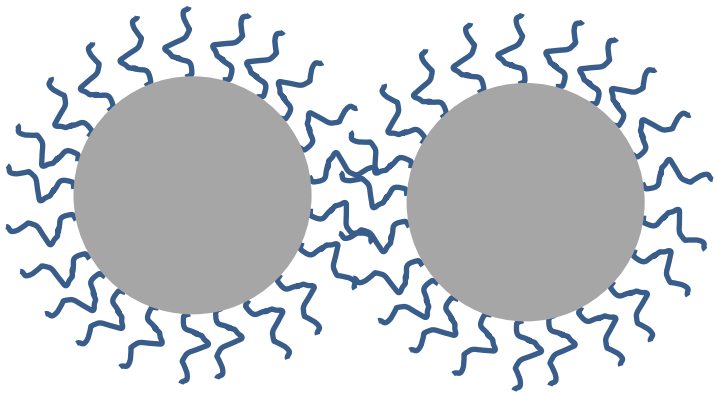


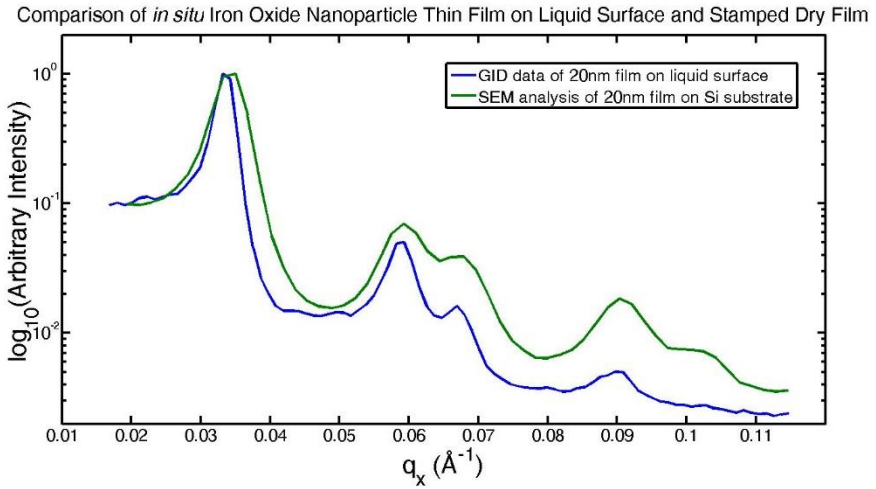
Thorek, D.L.J., *et. al.* (2006). *Annals of Biomedical Engineering* , 34(1).

SEM Measurements

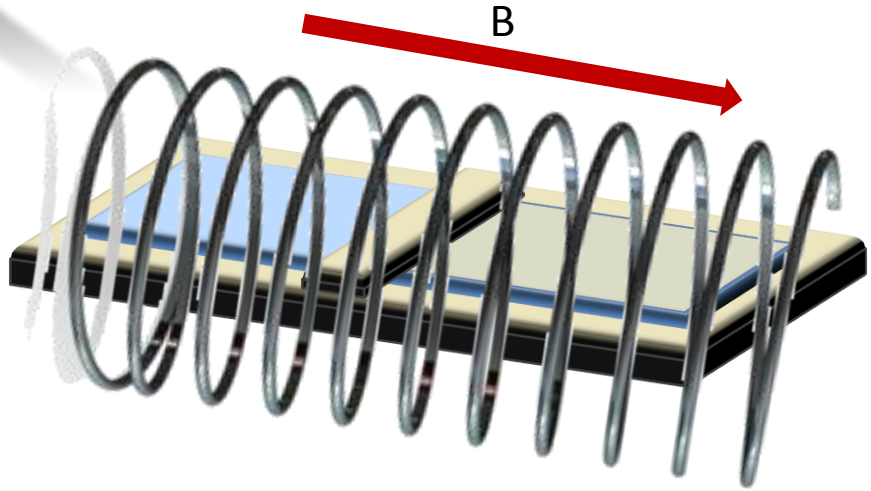


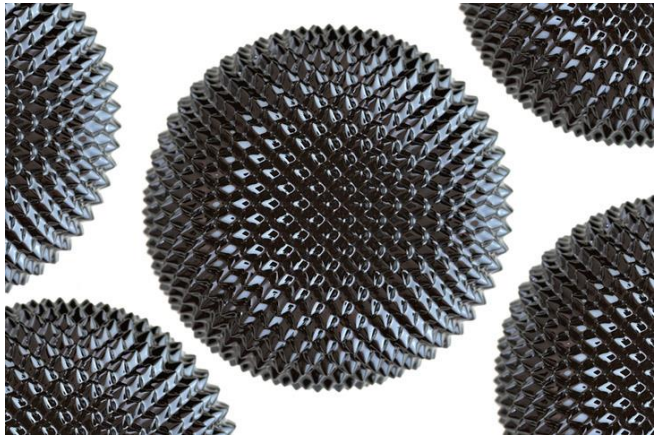
- Directed Self-Assembly?
  - Field On During Deposition
  - Field Off During Deposition

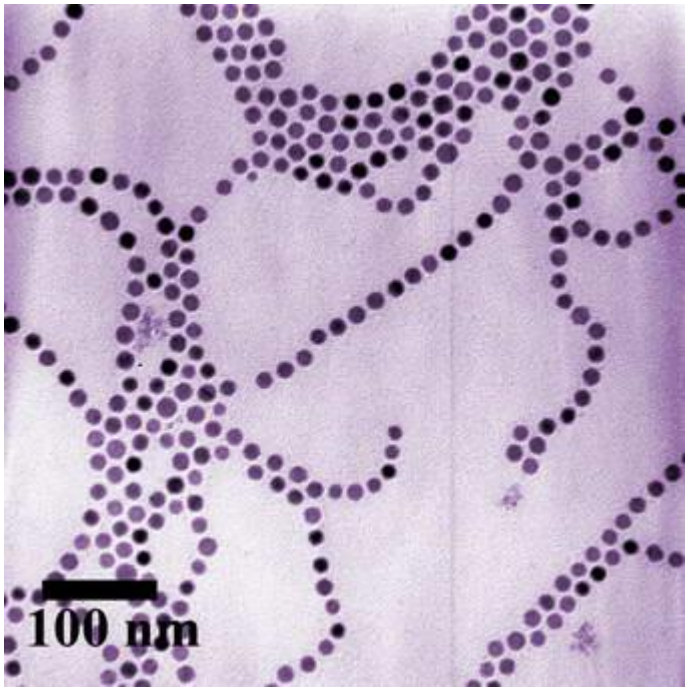




Dynamics Measurements







Kinge, S., Crego-Calama, M., & Reinhoudt, D.N. (2008). *ChemPhysChem*, 9(1).

Cheng, G., *et al*, (2005). *Langmuir* 21(26).

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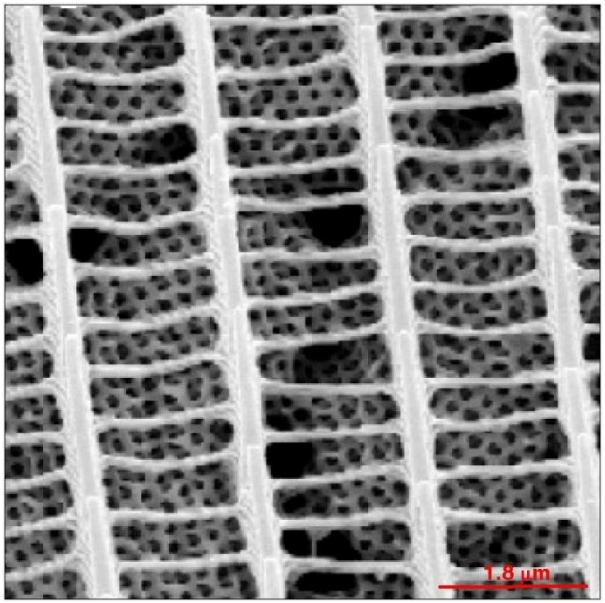
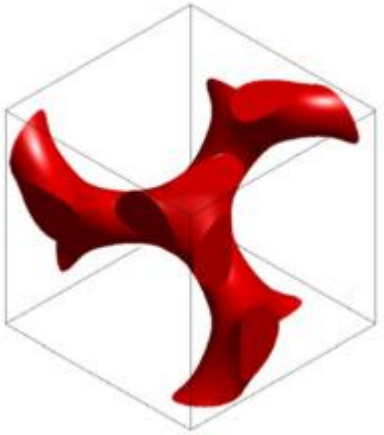
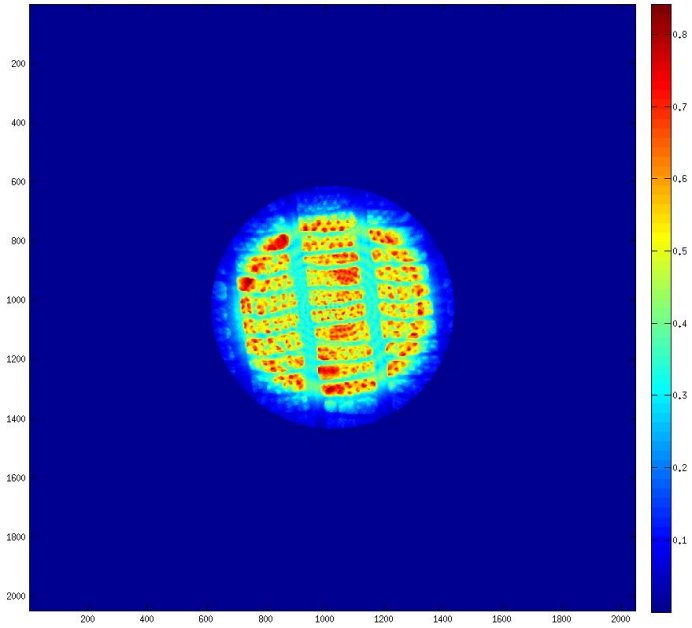
Butterfly Wing Coloration

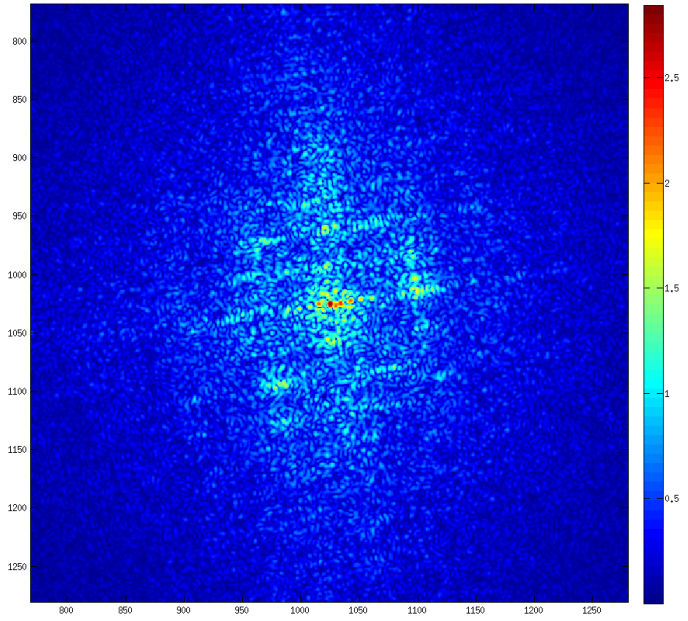




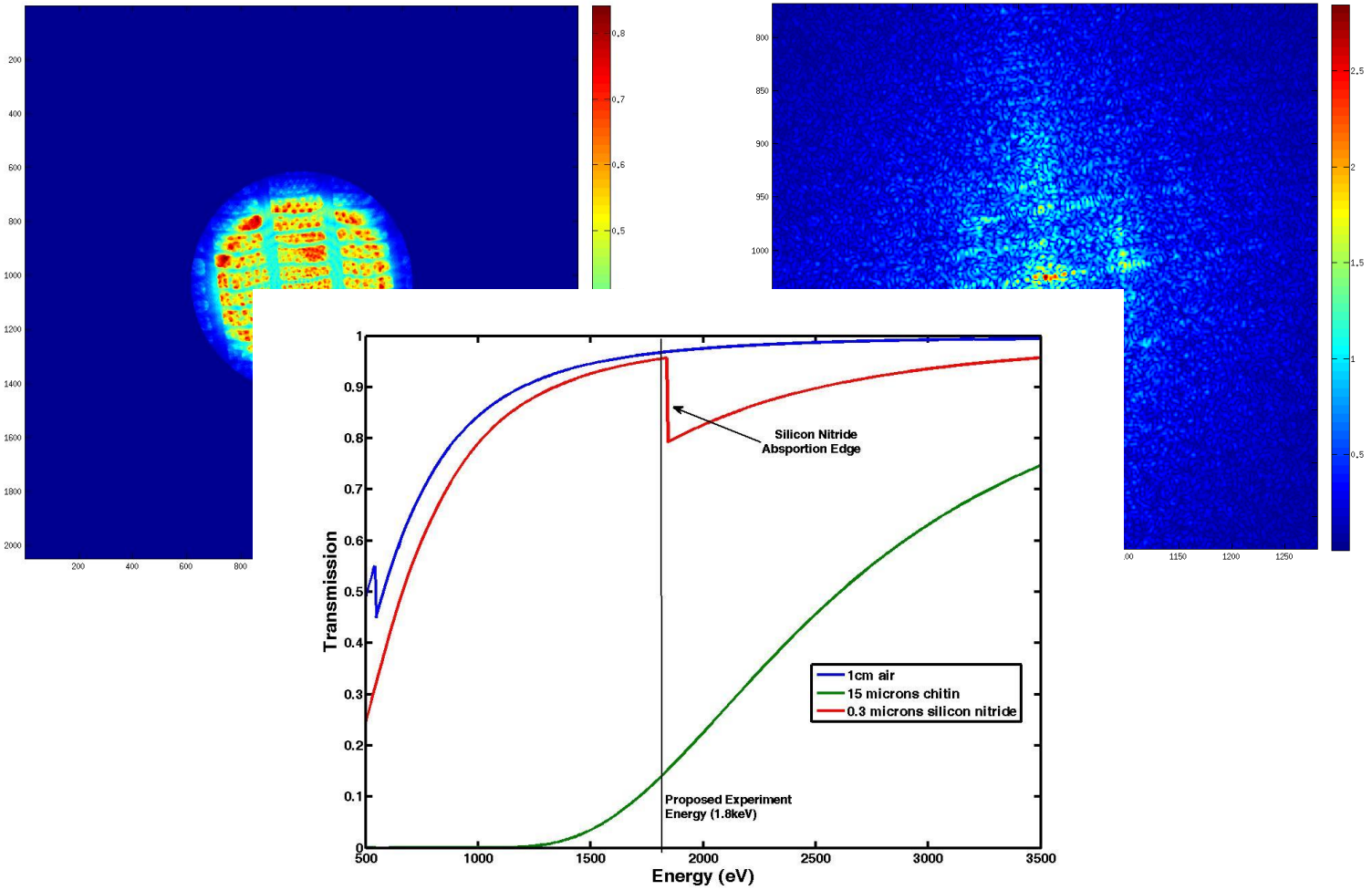
Saranathan, V., *et al*. (2010). *Proceedings of the National Academy of Sciences*, 107 (26).

X-Ray Coherent Diffractive Imaging (XCDI)





X-Ray Coherent Diffractive Imaging (XCDI)



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- Jacob Stanley
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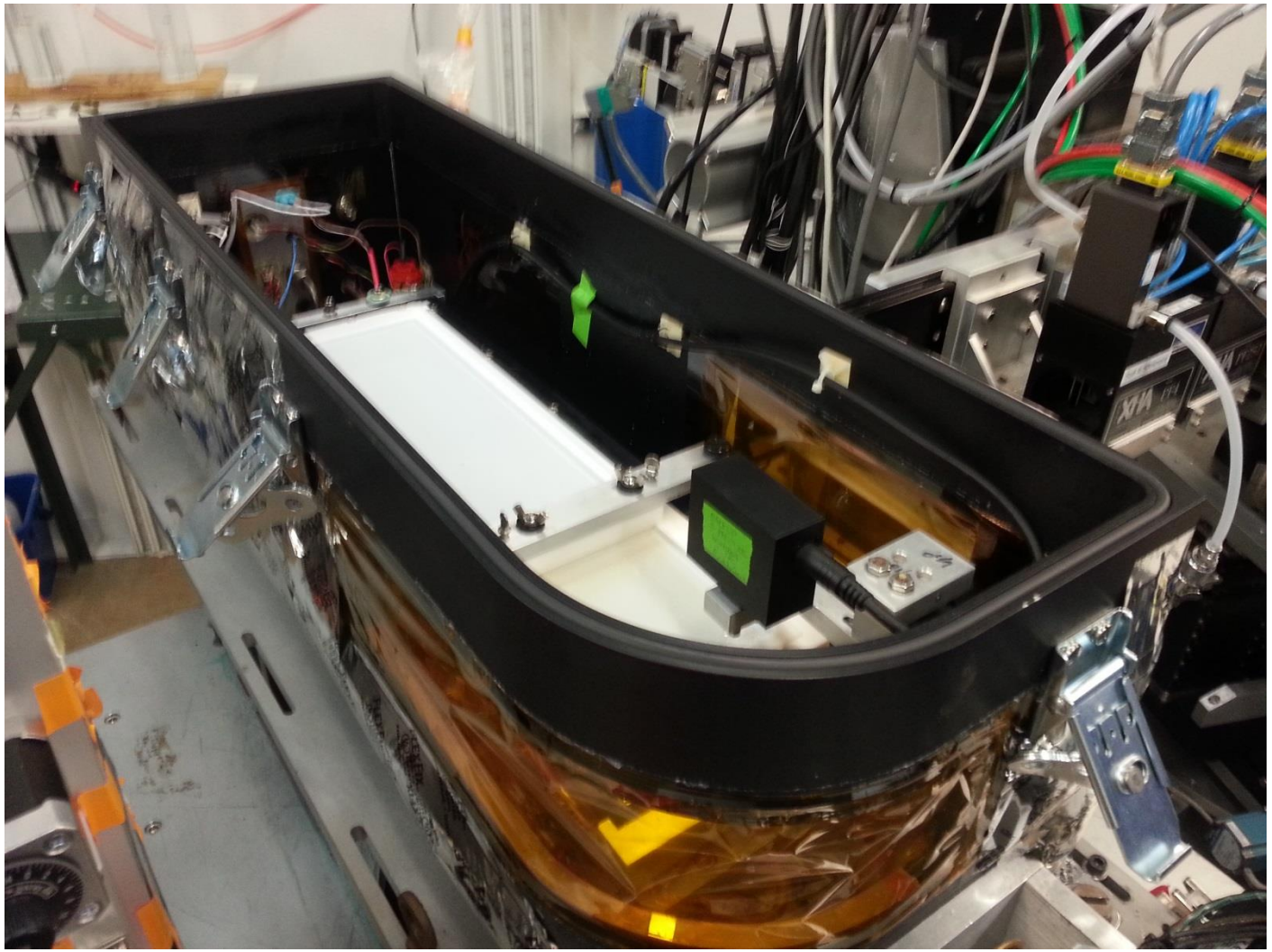
- Zhang Jiang (APS/S8)
- Suresh Narayanan (APS/S8)
- Alec Sandy (APS/S8)

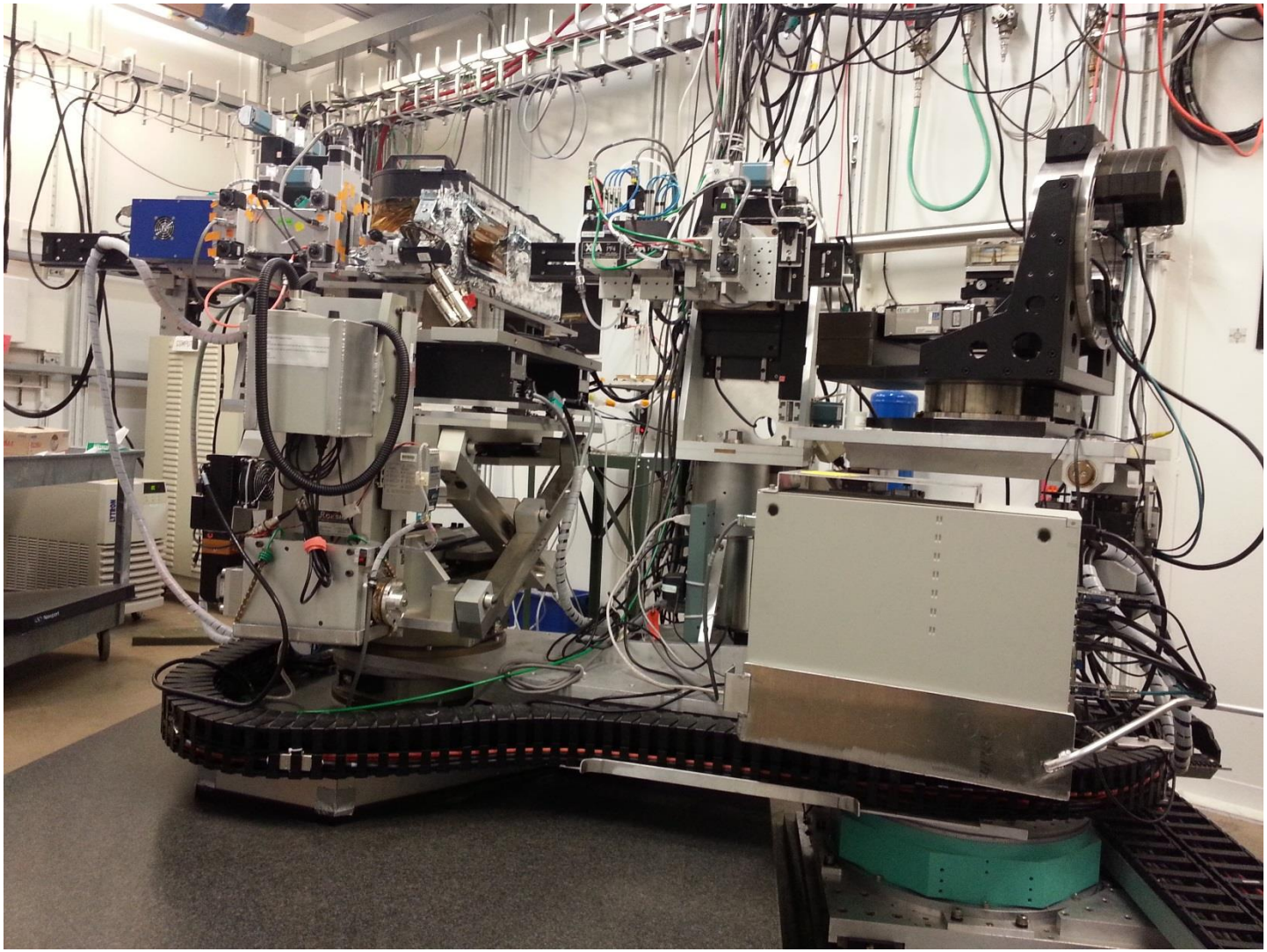
Thank You!

Backup Slides

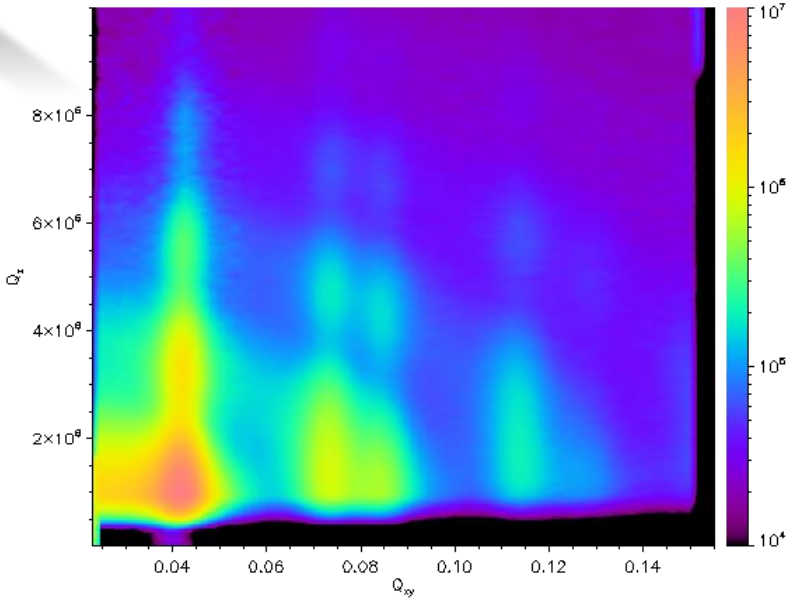
Langmuir-Blodgett Trough

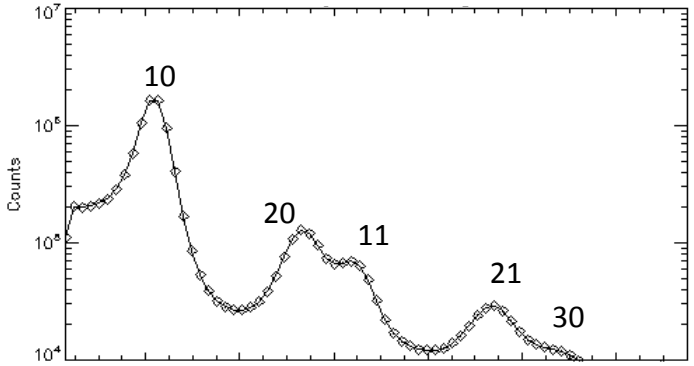


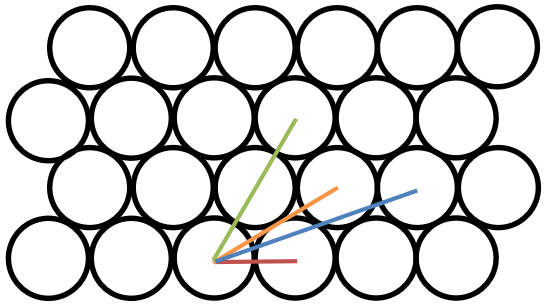
Liquid Surface Spectrometer



In-Plane Film Structure



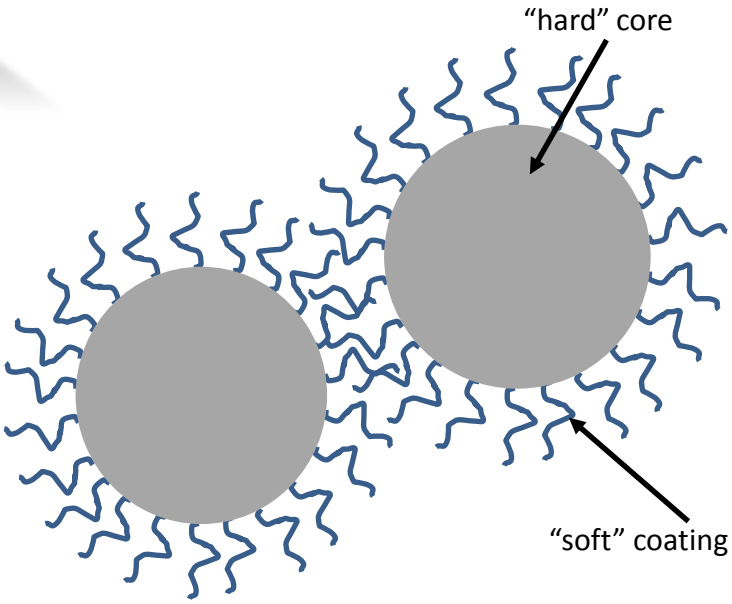




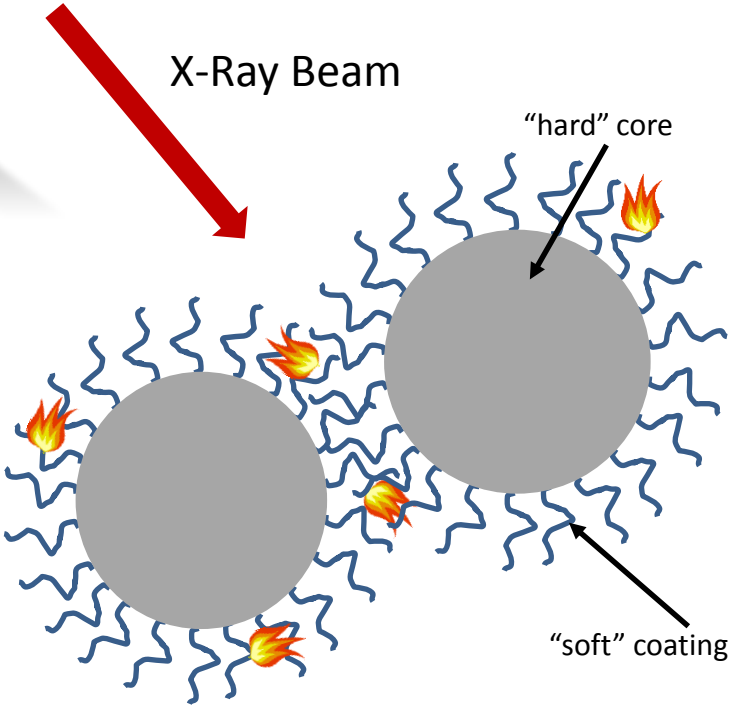
Nearest Neighbor Spacing

	1st	2nd	3rd	4th
Hexagonal Close Packed	1	$\sqrt{3}$ ≈1.73	2	$\sqrt{7}$ ≈2.65
Experiment	1	1.75	2.01	2.74

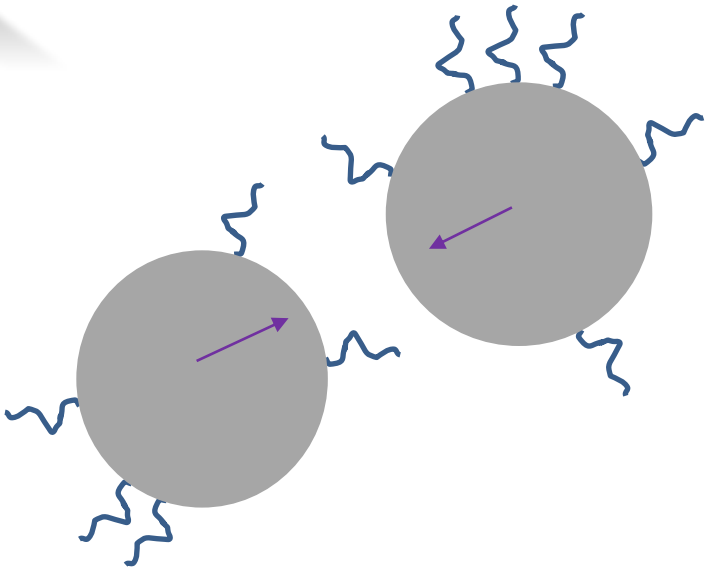
Radiation Damage



Radiation Damage



Radiation Damage



Radiation Damage